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Inorganic Chemistry Seminar Abstracts

1966-1967

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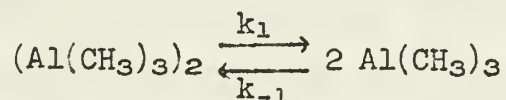
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ORGANOMETALLIC EXCHANGE REACTIONS OF GROUP III ALKYL

Kenneth C. Williams

June 27, 1966

The nature of the association of the trialkyl derivatives of the metals of group III in solution has been elucidated. It now appears that aluminum is the only member of this group whose saturated alkyl derivatives are associated in solution.¹ Trimethylaluminum is dimeric in hydrocarbon solutions.² Muller and Pritchard³ confirmed the bridge structure by the observation of two peaks in the nuclear magnetic resonance (n.m.r.) spectrum of trimethylaluminum in cyclopentane at -75°C. At room temperature they observed only one n.m.r. peak due to either intramolecular or intermolecular exchange of methyl groups. They estimated the Arrhenius activation energy for the exchange to be between 6 and 14 kcal/mole, and postulated that the exchange occurs by an intramolecular process. They suggested two possible mechanisms: (1) the breaking of one Al-C bond which may re-form with a different methyl group in the bridging positions or (2) the deformation of the molecule in which no bonds are broken, leading to a structure having four bridging methyl groups at the corners of a square. Ramey and co-workers⁴ did a more quantitative study on the temperature dependence of the n.m.r. spectra of a number of aluminum alkyl dimers in an attempt to elucidate the mechanism by which the alkyl groups are transferred from the bridging to terminal positions. For $(Al(CH_3)_3)_2$ the enthalpy of activation for the exchange was found to be 15.6 ± 0.2 kcal/mole. These authors postulated that the monomer was probably not formed as an intermediate but that the process is an intramolecular one involving the rupture of one Al-C bond, which then re-forms with a different alkyl group in the bridging position. Poole and co-workers have studied trialkylaluminum compounds using aluminum-27 n.m.r. They interpreted Muller and Pritchard's data as an intermolecular process according to the equation



Several investigators have studied the exchange of alkyl groups between mixed trialkyls of aluminum.^{4,6,7}

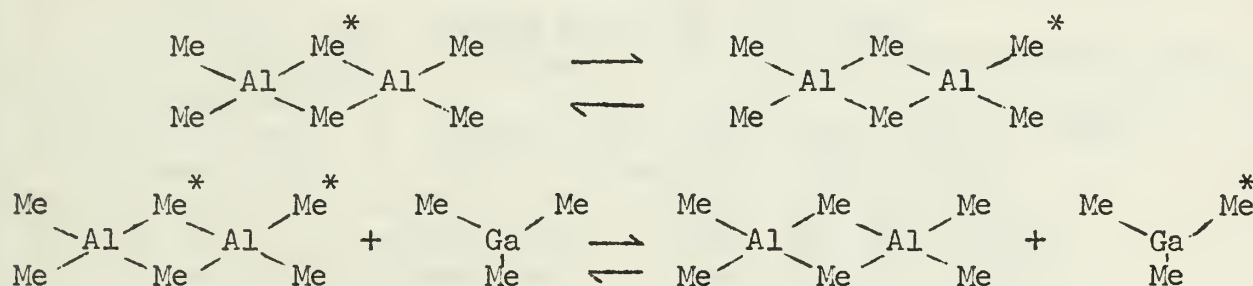
McCoy and Allred⁸ observed that methyl groups in solutions of trimethylaluminum and dimethylcadmium undergo a rapid intermolecular exchange at room temperature. By assuming a second-order process they were able to estimate an upper limit for the average lifetime of a methyl group before exchange.

Mader and Evans⁹ studied the intermolecular exchange of methyl groups in solutions of trialkylthallium compounds. They found that the exchange of methyl groups in trimethylthallium follows second-order kinetics and has an activation energy of 6.3 ± 0.5 kcal/mole in toluene.

Several investigations of exchange reactions of group III alkyls in basic solvents have been conducted^{10,11,12,13} but all the systems discussed in this seminar will be concerned with hydrocarbon solvents.

(CH₃)₃Ga-((CH₃)₃Al)₂ and (CH₃)₃In-((CH₃)₃Al)₂ Systems in Cyclopentane

The n.m.r. spectrum of a mixture of trimethylaluminum and trimethylgallium in cyclopentane consists of only a single peak at room temperature and, in view of the difference of chemical shifts of the pure compounds, indicates intermolecular exchange of methyl groups. At -60°C three proton resonances are observed which corresponds to the trimethylaluminum bridge and terminal groups and trimethylgallium. The exchanges going on at room temperature may be represented as



The activation energy for the exchange of methyl groups of trimethylgallium and trimethylaluminum dimer is 15.9 ± 0.5 kcal/mole and the expression for the rate constant is given by the equation

$$k = (3/2) (1/\tau_{\text{Me}_3\text{Ga}}) \frac{[\text{Me}_3\text{Ga}]}{[(\text{Me}_3\text{Al})_2]}$$

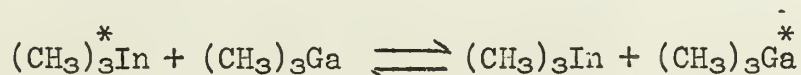
Due to the low solubility of trimethylindium in cyclopentane at low temperature quantitative data could not be obtained for the system (CH₃)₃In-(CH₃)₃Al)₂. However, some data on dilute solutions indicates the same kinetics are obeyed in the (CH₃)₃Ga-((CH₃)₃Al)₂ system.

(CH₃)₃Ga-((CH₃)₃Al)₂ and (CH₃)₃In-((CH₃)₃Al)₂ Systems in Toluene

In toluene the kinetics were the same for both systems and the activation energies and the rate expressions were the same as in cyclopentane. It was also shown that the kinetics for the exchange of bridge and terminal groups in trimethylaluminum is the same in toluene and cyclopentane, and it was found that the exchange is independent of trimethylaluminum concentration.

(CH₃)₃Ga-(CH₃)₃In System in Toluene

Low-temperature studies on samples containing equal amounts of (CH₃)₃Ga and (CH₃)₃In showed no significant line broadening. This result indicates the exchange



is very rapid and proceeds through a low-energy pathway, probably through a bimolecular process.

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SOME ASPECTS CONCERNING MOLECULAR ORBITAL CALCULATIONS

Anton Schreiner

July 12, 1966

The prediction of molecular properties has long been of interest to chemists. The several molecular orbital (MO) theories have been one approach, and aspects of some of these theories will be discussed in this seminar along with new features and findings.

The nature of MO calculations can be viewed as belonging to one of three levels. At the first level, one computes explicitly the expectation values of all electron-electron, electron-nuclear, and kinetic energy operators in Roothaan's¹ matrix element

$$F_{nk} = (n/k) + \sum_{j=1}^N \sum_{p=1}^M \sum_{q=1}^M C_{pj}^* C_{qj} [(nk/pq)(nq/pk)] \quad (1)$$

$$\text{where } (nk/pq) = \int X_n^*(1) X_k(1) \frac{1}{r_{12}} X_p^*(2) X_q(2) \cdot d\mathbf{v}(1) d\mathbf{v}(2) \quad (2)$$

$$\text{and } (n/k) = \int X_n^*(1) \left(-\frac{1}{2} \nabla_1^2 - \sum_{\alpha} \frac{Z_{\alpha}}{r_{1\alpha}} \right) X_k(1) d\mathbf{v}(1) \quad (3)$$

C is defined by

$$\phi_i = \sum_{k=1}^M C_{ki} X_k \quad (4)$$

This matrix element is required in the familiar equation

$$\sum_{k=1}^M C_{ki} (F_{nk} - E_i S_{nk}) = 0 \quad (5)$$

where

$$S_{nk} = \int X_n^*(1) X_k(1) d\mathbf{v}(1) \quad (6)$$

The amount of time required to evaluate the many integrals that arise prohibits the application of this method to large molecules, and approximations are necessary.

Considerable labor is saved by considering only the molecular valence electrons (second and third levels). This implies that molecular properties are dependent either on all electrons involved in bonding or on pi-electrons only, depending on molecule and/or theory. Theories in the valence electron framework generally differ in the method of integral evaluation (equation 2, for example), that is, whether the evaluation is explicit, empirical, or approximate, and can also differ by the type of terms assumed zero (see references 2 to 12, for example).

Two methods that treat all valence electrons are the Hoffmann⁸ method and an extension, the Van der Voorn version.⁷ Aspects of both will be discussed, limitations of the Hoffmann approach pointed out in view of new investigations.^{9,11} An analysis in terms of theories known for some time and new suggestions resulting from this analysis will be made. Some results will be given and some conclusions drawn.

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INTERACTIONS OF THE PERCHLORATE ANION

R. B. Gayhart

July 19, 1966

Introduction

A basic assumption in numerous studies in kinetics, electrochemistry, and complexation has been that the perchlorate anion does not directly interact with other species in solution. However, ion pairing and coordination by the perchlorate ion have been observed, as will be shown in this seminar.

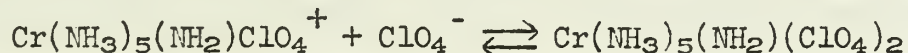
Ion pairing involves electrostatic attraction of two charged species separated by a distance greater than ordinary bonding distance (e.g. $[\text{Co}(\text{NH}_3)_6]\text{I}^{2+}$). Bjerrum¹ arbitrarily specified that ions of a 1:1 electrolyte in aqueous solution at 25° which were closer than 3.57 Å form an ion pair. At that distance, electrostatic attraction would enable the pair to survive several collisions with neighboring molecules and ions. The ions involved in ion pairing undergo only very minor perturbations on their structure, i.e., the perchlorate ion retains its tetrahedral symmetry with characteristic infrared and Raman absorptions. However, charge transfer bands in the ultraviolet spectrum are quite often shifted to lower energy. Ion pairing may also be observed by changes in kinetics of reaction, conductivity, solubility, potentiometry and NMR spectra.²

Coordination, on the other hand, involves close approach (ca. 2-3 Å) of the two interacting species, causing, in the case of the perchlorate anion, a lowering of symmetry and consequent alteration of the vibrational spectrum as well as other effects.

Ion Pairs

The phenomenon of ion pairing would be expected to become more probable as the dielectric constant of the solvent decreases. The suppression of β-diketone chelate formation for a number of cations in a 75 volume percent dioxane-25 volume percent water solution was interpreted in terms of perchlorate association.³

The rate of exchange of ammonia in hexamminechromium (III) perchlorate in liquid ammonia ($\epsilon = 22$) changes markedly as the perchlorate ion concentration was varied, suggesting the presence of an ion pair and the equilibrium



where the neutral complex was less reactive than the charged one.⁴

The variation of the extent of hydrolysis of ferric ion at constant ionic strength was interpreted by Sykes⁵ as evidence for a ferric-perchlorate ion pair. The association constants at 25° at ionic strengths of 0.025 and 0.437 were estimated to be 6.7 ± 0.7 and 3.7 ± 0.7 l-mole.

Conductivity studies of copper (II) perchlorate, where equivalent conductance was extrapolated to infinite dilution, revealed deviation from the Onsager relationship which was ascribed to the formation of the ion pair CuClO_4^+ with limiting dissociation constant of 0.9.

Dissociation constants for chloropentamminecobalt (III) perchlorate ion pairs at 25° and 35° have been determined from solubility measurements (0.07 and 0.09, respectively).⁷

The near ultraviolet spectra of aqueous solutions of cerous perchlorate together with perchloric acid and sodium perchlorate exhibited new peaks

which were attributed to the formation of a CeClO_4^{2+} complex. ΔS° for the formation of this complex was calculated as -31 e.u. This large negative value of ΔS° was taken as evidence for the formation of an ion pair rather than an "inner sphere" complex.

NMR indicated ion pairing of perchlorate anion and p-chloroanilinium ions in dimethyl sulfoxide and dioxane solutions. It was shown that the shape of the absorption line for an anilinium ring proton depends upon the anion in solution and that the line shape, being rather complicated for iodide anion, becomes simpler as the series iodide, bromide, fluoride, perchlorate, tetrafluoborate is traversed. Position of the lines lead to the postulation of formation of ion pairs.⁹

Alei¹⁰ observed paramagnetic shifts in the NMR peak of oxygen-17 for labile H_2O and perchlorate anion in aqueous acidic solutions of the rather inert $[\text{Cr}(\text{H}_2\text{O}^{16})_6]^{3+}$. These shifts were attributed to ion pairing.

Coordination Compounds

Some indication of the coordinating ability of the anion of any acid can be gained by determination of the dissociation constant of the acid. Perchloric acid is almost completely dissociated in aqueous solution, pK_a being -7.0.¹¹

This weak coordinating ability of perchlorate anion may be explained in terms of the π -bonding character of the Cl-O bond. The order of decreasing chemical reactivity $\text{IO}_3^- > \text{BrO}_3^- > \text{ClO}_3^-, \text{ClO}_4^-$ parallels the shortening of the X-O bond from that which is expected for the single X-O bond. As π -bonding (i.e., electron donation from the oxygen atom to the p and vacant d orbitals on chlorine) decreases the availability of p orbitals on oxygen for bonding, chemical reactivity decreases.^{12,13} Appreciable π -bonding in the perchlorate anion has been indicated by measurements of bond order using Raman spectroscopy.¹⁴

Raman studies of aqueous solutions of perchlorates of 17 metal ions yielded tentative identification of complexation for only Thallium (I), Magnesium (II), and Manganese (II). The lines associated with the complexes were extremely weak.¹⁵ Similar and more recent work by Plane and Hester¹⁶ showed no indication of complexation in near-saturated aqueous solutions of metal perchlorates.

Paramagnetic shifts in the NMR absorption of oxygen-17 in perchlorate anion and water were observed in aqueous solutions of chromium (II) ion. As the concentration of perchlorate anion was increased, the shift in the H_2O^{17} absorption was reduced and finally changed sign. This effect was ascribed to the replacement by perchlorate ions of water molecules from the coordination sphere.¹⁷

The chlorine-35 NMR absorptions of perchloric acid solutions of various metal ions (viz., Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Ce^{3+} , and Be^{2+}) were studied by Klanberg, *et al.*¹⁸ Broadening of the absorption was observed only in the case of the manganese (II) solution, indicating the formation of a weak inner-sphere complex. Since chlorine-35 is separated by an oxygen atom in the perchlorate anion, some covalent character would seem to be required in the bonding of this manganese complex.

Jones and Bjerrum¹⁹ studied the ultraviolet spectrum of hexaquo-chromium (III) perchlorate in strong perchloric acid solutions. A time-dependent change in the spectrum of the solution was taken as evidence for the formation of the monoperchloratochromium (III) ion.

Coordination of perchlorate anion should bring about changes in the vibrational spectrum of the ion. Minor shifts or splitting may be attributed

to lowering of site symmetry, coupling of vibrations of the perchlorate groups within the same unit cell, or an isotropic effect within the ion. All these may be observed in perchlorate salts. Considerably greater splitting in the infrared bands can only be explained in terms of actual coordination of the ion. Assignments of peaks produced by splitting of degenerate tetrahedral frequencies were made by analogy to similar and previously assigned compounds. For the lowering of symmetry, T_d to C_{3v} to C_{2v} , the changes in spectra in going from $HClO_4$ to ClO_3F and SO_4^{2-} to SO_2F_2 were examined.²⁰

Hathaway and Underhill²¹ isolated the following complexes: $Cu(ClO_4)_2 \cdot 4CH_3CN$ and $Cu(ClO_4)_2 \cdot 2.5EtOAc$. Infrared spectra of these compounds indicated monodentate coordination.

The same authors²⁰ gave further examples of monodentate coordination as well as bidentate coordination. The complexes $Co(ClO_4)_2 \cdot 6CH_3CN$, $Mn(ClO_4)_2 \cdot 4CH_3CN$, and $Zn(ClO_4)_2 \cdot 4CH_3CN$ were reported along with infrared evidence which supports monodentate perchlorate coordination. Similar evidence was presented for perchlorate coordination in the lower hydrates of iron (III), nickel (II), and copper (II) perchlorates. Anhydrous copper (II) and iron (III) perchlorate infrared spectra may be interpreted as indicating C_{2v} symmetry. However, the splittings observed in the copper complex were rather small, and could also be interpreted as isotopic effects or coupling of the vibrations of the two perchlorate anions.

Hathaway, et al.,²² contended that the perchlorate anion was involved in covalent bonding in the dihydrates of manganese, cobalt and nickel perchlorate. (A recent publication concerning nitronium perchlorate reports similar infrared spectra and maintains that spectra can be explained by purely ionic interactions.²³) Infrared spectra, visible spectra and magnetic susceptibility measurements supported bidentate perchlorate coordination.

Wickenden and Krause²⁴ prepared acetonitrile complexes of nickel and observed infrared evidence for perchlorate coordination. Bidentate coordination of perchlorate was shown by the splitting of the C_{3v} peaks observed in the spectrum of $[Ni(CH_3CN)_2(ClO_4)_2]$. Electronic spectra and magnetic data supported an octahedral environment for nickel in both complexes.

Perchlorate coordination in pyridine and substituted pyridine complexes has been investigated by several groups. Moore, et al.,²⁵ reported monodentate perchlorate complexes of the type $[Ni(X-py)_4(ClO_4)_2]$ where X is 3-bromo, 3,5-dimethyl, and 4-isopropyl. Visible spectra indicated distortion octahedral configuration.

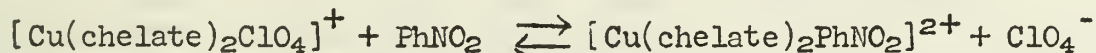
Rosenthal and Drago have reported preparation of $[Ni(py)_4(ClO_4)_2]$. Nujol-mull infrared spectra showed that the anions were monocoordinated. Electronic spectra were characteristic of tetragonal distortion. The conductance of a dichloromethane solution of the complex indicated that no ionic species were present.²⁶ The very tetragonal configuration of this complex enabled it to undergo a reaction in the solid state when suspended in chloroform, removing the perchlorate ions from the coordination sphere, and resulting in a spin-paired compound $[Ni(py)_4](ClO_4)_2 \cdot CHCl_3$, which contains only tetrahedral perchlorate ions.²⁷

Vallerino, et al.,²⁸ prepared nickel (II) complexes of 2-, 3-, and 4-picoline, but found perchlorate coordination only in the case of $[Ni(3-pic)_4(ClO_4)_2]$. The infrared spectrum indicated monodentate perchlorate and the electronic spectrum supported a tetragonal complex. The weakness of the perchlorate coordination was indicated by the ease with which the non-ionic tetragonal compound changed partially in dichloromethane solution to yield square planar $[Ni(3-pic)_4](ClO_4)_2$ (indicated by spectra) in the ratio 80% tetragonal to 20% square planar complex.

W. R. McWhinnie²⁹ prepared $[\text{Cu}(\text{en})_2(\text{ClO}_4)_2]$ by treating copper (II) perchlorate with excess ethylenediamine in absolute ethanol. The spectrum of the complex indicated monodentate perchlorate anion.

S. F. Pavkovic and D. W. Meek³⁰ synthesized three perchlorate complexes of the type $[\text{Ni}(\text{amine})_2(\text{ClO}_4)_2]$ (where amine = N-methyl-, N,N'-dimethyl-, and N,N,N'-trimethylethylenediamine). Spectra indicated bidentate perchlorate only in the N,N,N'-trimethyl substituted complex.

Perchlorate coordination in the bis-chelate complexes $[\text{Cu}(\text{chelate})_2(\text{ClO}_4)_2]^+$ (chelate = bipyridyl and o-phenanthroline) was indicated by weak electrolyte behavior in nitrobenzene, which was attributed to the equilibrium



Conductometric data yielded a stability constant of 10^3 for the bipyridyl complex. Coordination of perchlorate ion was shown by the effect of additional perchlorate ion on the visible spectrum of $[\text{Cu}(\text{bipy})_2](\text{PF}_6)_2$, where its broad absorption band was shifted to longer wavelength.³¹

Perchlorate coordination has also been observed in complexes of phosphines and arsines and their oxides. Dyer, *et al.*,³² found strong perchlorate coordination in trigonal pyramidal nickel (II) complexes $[\text{Ni}(\text{chel})(\text{ClO}_4)]\text{ClO}_4$ with such quadridentate chelates as tris(o-diphenylphosphinophenyl)phosphine and its arsenic analog. Coordination of the anion was demonstrated by conductance studies and infrared spectra. The spectrochemical series in the arsenic ligand complexes is of some interest:



The perchloratodiphenylarsineoxide complexes of manganese, cobalt, nickel and zinc were obtained by Lewis, *et al.*,³³ from alcoholic solutions of the arsine oxide and the metal perchlorate. The structure of the cobalt complex is reported by P. Pauling, *et al.*³⁴ While the infrared spectrum indicated both coordinated and uncoordinated perchlorate, the x-ray analysis shows that even the coordinated perchlorate ion is strictly tetrahedral within experimental error.

F. A. Cotton and D. L. Weaver³⁵ determined the structure of bis(perchlorato)bis(2,5-thiahexane)cobalt(II) by single crystal x-ray diffraction. The Co-O distance (2.34 Å) suggested rather weak bonding. The infrared spectrum indicated monodentate perchlorate.

Trimethyltin perchlorate was synthesized by dissolving anhydrous silver perchlorate and trimethyltin bromide in methanol, filtering off the resultant silver bromide, and then removing the solvent in vacuo at 120°. The infrared spectrum indicates bidentate perchlorate and a bridging structure is proposed.³⁶

D. K. Straub and Y. M. Yung isolated the first anionic complexes containing perchlorate as the only ligand.^{37, 38} All complexes contained some excess tetrabutylammonium or methyltriphenylarsonium perchlorate, according to elemental analysis and infrared spectra (which showed both coordinated and uncoordinated perchlorate). Electronic spectra support tetrahedral coordination for the cobalt complex, octahedral coordination for the nickel complex (with both mono- and bidentate perchlorate) and tetragonally distorted octahedral coordination for copper.

I. E. Starik and V. I. Amperogova³⁹ determined the overall formation constants of $\text{Po}(\text{ClO}_4)_n^{4-n}$ using solvent extraction data. The formation constants were 0.13, 3.3×10^{-2} , 9.0×10^{-3} , and 1.6×10^{-3} for $n = 1, 2, 3, 4$, respectively.

Conclusion

Perchlorate anion has been shown to be capable of interaction with metal ions in solution and in solid complexes. In almost every case, however, coordination took place only under the most favorable conditions (i.e. high perchlorate concentration, insufficient number of ligands in the coordination sphere, etc.), demonstrating the rather small capacity for coordination by this anion.

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EXTENDED HÜCKEL THEORY

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INTRODUCTION

In recent years inorganic chemists have become increasingly interested in the electronic structure of their compounds. Theoretical approaches have therefore been adopted in order to rationalize a large amount of experimental data such as electronic spectra, dipole measurements, and various properties of the molecules. This has led to a great deal of work in crystal field theory and ligand field theory for complexes and also to activity in various types of molecular orbital theory. One approach to molecular orbital theory which incorporates experimental data is becoming more and more popular with inorganic chemists. This is referred to as semiempirical molecular orbital theory.¹ The foundations for semiempirical molecular orbital theory were first published by Mulliken in 1949.² The first practical use of it was made by Wolfsberg and Helmholz in an attempt to explain the electronic spectra of MnO_4^- , CrO_4^- , and ClO_4^- .³ Much work has been done recently on transition metal complexes. In 1962 Hoffmann and Lipscomb^{4,5} developed a semiempirical method capable of treating all kinds of molecules, which is called extended Hückel theory. A good deal of inorganic research has been done in the last few years using this method of molecular orbital calculation. It is the purpose of this seminar to give a description of the extended Hückel theory, both the method of calculation and the results that can be obtained.

The essential feature of any semiempirical method is that the matrix elements of the secular determinant are not calculated by integration as would be done in an a priori SCF calculation, but instead are approximated by data obtained experimentally. This is absolutely necessary at the present time because only small molecules may be treated with a SCF calculation.

EXTENDED HÜCKEL THEORY

The simple Hückel⁶ theory has been widely used by organic chemists for calculations on the π systems of planar organic molecules. This system operates under the assumptions of complete σ - π separability and zero differential overlap. In the extended Hückel theory of Hoffmann and Lipscomb, the above two approximations are abandoned. This method allows a relatively simple calculation of the basic properties of all types of inorganic and organic structures, treating σ and π interactions in the same calculation. The extended Hückel theory succeeds in just those areas where simple Hückel theory does such as charge distributions but performs poorly in other areas such as spectral predictions.

Using the ordinary LCAO approach, a molecular orbital can be expressed as a linear combination of atomic orbitals.

$$\psi_i = \sum_j C_{ij} X_j$$

Here the X_j 's are Slater atomic orbitals.^{7,8} Upon minimizing the total energy with respect to the coefficients one can easily obtain the familiar set of secular equations

$$\sum_{i=1}^N [H_{ij} - ES_{ij}] C_{ij} = 0 \quad j = 1, 2, \dots, N.$$

The complete secular determinant is treated, all interactions accounted for, and all off diagonal terms are retained. In the secular equation, S_{ij} is the familiar overlap matrix between 2 orbitals. Tables of these have been published or a computer program can calculate them from known formulas if given the atomic coordinates and the exponential constants in the Slater orbitals.

At this point use is made of experimental data to approximate the various integrals in the Hamiltonian matrix. The diagonal terms, $H_{ii} = \int \phi_i H \phi_i dt$, cannot be explicitly calculated and must be estimated. H_{ii} corresponds to the Coulomb integral (from simple Hückel theory) for some atomic orbital in the molecule. An atom in a molecule is assumed to have very nearly the same electron configuration as it would have in its valence state. (VanVleck⁹ has defined the valence state as the hypothetical "state" of an atom in which the interaction of the electrons of the atom are as nearly as possible the same as they would be if the atom were part of a molecule.) Therefore the H_{ii} can be thought of as the energy of the orbital ϕ_i when the atom is in the valence state. The valence state ionization potential of an orbital is a measure of the energy needed to remove an electron from an orbital in the valence state to infinity. This valence state ionization potential is, then, a reasonable estimation of the energy of an orbital in the molecule. A great deal of theoretical work has been published on valence state ionization potentials and tables are found in several places.¹⁰ The valence state ionization potentials are dependent on charge, and, as will be seen later, it is necessary to specify the charge when doing a calculation.

The crucial choice in the extended Hückel calculation is the choice of the off diagonal Hamiltonian terms. Unfortunately, this is at present the weakest part of the method because there is no sound theoretical way to show how these off diagonal elements may be obtained. In 1949 Mulliken² proposed that the off diagonal terms in a molecular orbital calculation on a diatomic molecule be approximated by

$$H_{ij} = \int \phi_i H \phi_j dt = K/2 S_{ij} (H_{ii} + H_{jj}).$$

This was proposed using a certain amount of intuition based on symmetry arguments. In the above expression $S_{ij} = \int \phi_i \phi_j dt$ is the usual two atom overlap integral. H_{ii} and H_{jj} are the appropriate valence state ionization potentials and K is a constant chosen so that calculated energy level differences are reasonable when compared with experiment. This formula for H_{ij} was later used in a calculation on MnO_4^- and is often used in the extended Hückel method. Another approximation has been suggested by Ballhausen and Gray^{1,11} using the geometric mean of the valence state ionization potentials rather than the arithmetic mean:

$$H_{ij} = K S_{ij} (H_{ii} H_{jj})^{1/2}$$

Recently another formula has been proposed by Cusachs:¹²

$$H_{ij} = 1/2 S_{ij} (H_{ii} + H_{jj}) (2 - |S_{ij}|).$$

This eliminates one of the arbitrary constants and has been suggested because it was observed that this approximation gave good results in a number of cases and has the correct asymptotic behavior. None of the above approximations have a rigorous theoretical foundation and this fact is one of the principle objections to extend Hückel theory.

In order to aid in understanding the method of calculation, a few lines will now be devoted to a general outline of the procedure. The calculation is performed by a computer using a program which was originally assembled by Hoffmann. The information needed for the calculation is the following: atomic coordinates for each atom,¹³ exponential constant for each Slater orbital in the basis set, atomic charges for each atom, and valence state ionization potentials for each orbital.

The first step is to calculate all of the interatomic distances in the molecule. Using these interatomic distances the assumed Slater exponents, each term in the overlap matrix is calculated using known formulas. (Overlap integrals are also given in tabular form as a function of distance and Slater exponent in various places.)¹⁴ Once the overlap matrix has been constructed, the Hamiltonian matrix can be set up. This is done using the input valence state ionization potentials as the diagonal elements and calculating the off diagonal terms using one of the formulas discussed previously. At this point all of the terms in the secular determinant are known. The secular equation can be solved with a symmetrical orthogonalization¹⁵ or a Gram-Schmidt orthogonalization followed by diagonalization of the resulting Hamiltonian matrix. Matrix diagonalizations are accomplished using the Jacobi method.

Once the secular equation is solved, one obtains the molecular orbitals in terms of the atomic orbital coefficients, and the energies for each. The total energy of the molecule is calculated by summing the energies of the filled molecular orbitals.¹⁶ The next step in the calculation is to perform a Mulliken population analysis¹⁷ on the molecular wavefunctions. From this one may obtain such information as atomic overlap population, reduced overlap population, and a charge distribution over the molecule. This charge distribution which is obtained from the population analysis is now compared with the initial charge distribution. If they are essentially the same, the calculation is complete. However, usually this charge distribution is different from the initial one and the calculation is repeated using a new assumed charge distribution. This procedure is then repeated until initial and final charges agree.

MULLIKEN POPULATION ANALYSIS

When one obtains a LCAO wavefunction, whether it be by a semiempirical or a SCF procedure, it is obviously of interest to draw as much physical insight as possible from the data. There are various systematic procedures for doing this, but probably the most common one is referred to as the Mulliken population analysis.¹⁷ In this process the electronic population is broken down into partial and total "gross atomic populations" or into partial and total "net atomic populations" along with overlap populations. Such information as degree of hybridization and gross charge on each atom can be obtained. The study of reduced overlap populations gives quantitative figures which may be taken as measures of bonding and anti-bonding strengths.

For the sake of demonstration consider a normalized diatomic LCAO molecular orbital, $\psi = C_a X_a + C_b X_b$. The m.o. ψ is occupied by N electrons (usually N=2). If we take ψ^2 times N the following equation is obtained.

$$N\psi^2 = NC_a^2 X_a^2 + 2NC_a C_b S_{ab} (X_a X_b / S_{ab}) + NC_b^2 X_b^2.$$

In this equation, S_{ab} is the overlap integral. If the above equation is integrated over all space, the following equation results.

$$N = NC_a^2 + 2NC_a C_b S_{ab} + NC_b^2.$$

NC_a^2 is called the "net atomic population" for atom a.

$2NC_a C_b S_{ab}$ is called the overlap population.

$NC_a^2 + NC_a C_b S_{ab}$ is the "gross atomic population" for atom a.

These equations can be extended quite easily to polyatomic molecules. From the atomic populations one can obtain the charge distribution in a molecule and these are the charges which are calculated in the Hoffmann program.

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SOME APPLICATIONS OF THE EXTENDED HUCKEL METHOD

A. Barrier to Internal Rotation in Ethane

Hoffmann has considered the barrier to internal rotation in ethane.^{5a} To determine this quantity, one calculates the difference in the total energy between the fully eclipsed conformation and the staggered conformation. From the results of such a calculation, one can get some information about the origin of the barrier. The difference in energies between the eclipsed and staggered conformations was calculated to be about 4.0 kcal/mole. This corresponds to an experimental value of about 2.7-3.0 kcal/mole and a value from a SCF calculation of 3.3 kcal/mole.

It was found that the prevailing contribution to the barrier comes from doubly degenerate orbitals. The highest filled level determines the direction of the barrier. From an inspection of the atomic orbital coefficients for the wavefunctions of ethane in the two conformations, it can be seen that these doubly degenerate orbitals are C-H orbitals composed of 1s hydrogen and 2p_x and 2p_z carbon atomic orbitals. In addition, an examination of the electron distribution shows a transfer of electrons from carbon to protons is associated with greater stability of the staggered form. The shape of the barrier was investigated and it was found that the equation $\Delta E = (2.01)(1 - \cos 3\theta)$ kcal/mole was followed with an absolute deviation of less than 1%. The results from these calculations agree reasonably well with a non-empirical calculation by Pitzer and Lipscomb.¹⁸

B. Phosphorous (V) Chlorofluorides

Van der Voorn¹⁹ has carried out extended Hückel calculations on the phosphorous chlorofluorides, PCl_nF_(5-n), in order to investigate the bonding in these molecules. He was able to predict the most stable isomer in each case. Experimentally it has been observed that F atoms tend to occupy the axial positions in preference to the equatorial ones. Previously an explanation for this has been that when the F is in an axial position there is strong P-F π -bonding which stabilizes these particular molecules. However, in this work there is some evidence which may lead one to believe that the isomers with an axial fluorine are more stable as a result of σ bonding.

The following molecules were investigated: PFCl₄, PF₂Cl₃, PF₃Cl₂, and PF₄Cl. The most stable isomers of the first three of these molecules have been determined by F¹⁹ n.m.r., infrared and raman, nuclear quadrupole resonance, and dipole moment measurements.^{20,22} The stable isomer of PF₄Cl has not been established. In every case the results of the extended Hückel calculations agree qualitatively with experimental data. For the PF₄Cl molecule the isomer with the axial F atom was predicted to be the most stable.

C. Porphyrin Complexes of Transition Metals.

Zerner and Gouterman²³ have carried out extended Hückel calculations on transition metal complexes of porphyrin with the metals Mn, Fe, Co, Ni, Cu, and Zn. With their model, they are able to discuss magnetic state, coupling of the ring and the metal, electronic transitions, and the effect of non-planarity of the ring. They used a basis set consisting of all the valence orbitals of H, C, and N and the 3d, 4s, and 4p of the metal.

From the results obtained, Zn and Ni are predicted to be diamagnetic; Co and Cu are of course paramagnetic and Co is predicted to have low spin. It has been found experimentally that the magnetic susceptibility of Co is temperature dependent.²⁴ The calculations show that for Co the four low lying metal d orbitals are split by no more than 0.04 e.v. As a result, the "electron hole" would be able to move among the 4 metal d orbitals.

A calculation on Ni was carried out with a pyridine molecule placed above the plane of the ring. This resulted in a considerable lowering of the high energy $d_{x^2-y^2}$ orbital and a raising of the d_{z^2} such that a paramagnetic species might result. It has been found experimentally that Ni porphyrins are paramagnetic in pyridine solutions.²⁵

Most of the results given up to this point show at least a qualitative agreement with experimental data. However, these data depend on the energies. The extended Hückel theory at the present level of sophistication appears to give very poor wavefunctions. This is reflected when a quantity depending on the wavefunctions is calculated and compared with experimental data. An example of this fact can be shown with some of the data on the metal porphyrins. The transition dipole strength is a quantity which depends on the wavefunctions. (The formula is $q^2 = e \langle \psi_i | \vec{r} | \psi_j \rangle$.) Looking at a typical set of data (Table I) one can see that the calculated energy of the $a_{2u} \rightarrow e_g$ and $a_{1u} \rightarrow e_g$ transitions agree well with experiment, but the calculated value of q^2 is very poor. This is a common downfall of recent extended Hückel calculations and is something which should be improved considerably.

Table I		
	Calculated	Experiment
$\Delta E(a_{2u} \rightarrow e_g)$	2.01 e.v.	
$\Delta E(a_{1u} \rightarrow e_g)$	2.35	
ΔE	2.18	2.19 e.v.
$q^2(a_{2u} \rightarrow e_g)$	9.61 \AA^2	
$q^2(a_{1u} \rightarrow e_g)$	10.10 \AA^2	
total q^2	19.81 \AA^2	5.16 \AA^2

D. Molecular Orbital Calculations of Spin-Spin Coupling Constants for Hydrocarbons

Pople and Santry²⁶ have developed a method of treating coupling constants with LCAO molecular orbital theory. The theory is able to calculate contributions from the three important mechanisms for spin-spin interaction. These are 1) electron spin-nuclear spin (spin dipolar) 2) nuclear spin-electron orbital (spin orbital) and 3) Fermi contact interactions. However, the spin dipolar and the spin orbital contributions are negligible if either of the nuclei involved are protons. In the case where a proton is involved, one need only consider the contact contributions to the spin coupling constant. Using this fact Fahey, Graham, and Piccioni²⁷ have used the extended Hückel theory to calculate a number of coupling constants in hydrocarbons.

In the one electron molecular orbital approximation, the contact contribution J_{AB} to the coupling of nuclei A and B is given by

$$J_{AB} = -\left(\frac{128}{9}\right) \pi \hbar^2 \gamma_A \gamma_B \sum_i^{\text{OCC}} \sum_j^{\text{UNOCC}} (\Delta E_{i-j})^{-1} (\psi_i | \vec{r}_A | \psi_j) (\psi_j | \vec{r}_B | \psi_i)$$

where β is the Bohr magneton, γ_A and γ_B are magnetogyric ratios, ψ_i is an occupied molecular orbital and ψ_j an unoccupied m.o., and finally δ is the Dirac delta. Once the LCAO approximation $\psi_i = \sum_{\mu} C_{i\mu} \phi_{\mu}$ has been introduced the equation becomes

$$J_{AB} = \left(-\frac{128}{9}\right) \pi \hbar \beta^2 \gamma_A \gamma_B \sum_i^{\text{OCC}} \sum_j^{\text{UNOCC}} (E_j - E_i)^{-1}$$

$$\sum_{\mu\sigma} C_{i\mu} C_{j\mu} C_{j\nu} C_{i\nu} (\phi_{\mu} | \sigma(r_A) | \phi_{\mu}) (\phi_{\nu} | \sigma(r_B) | \phi_{\nu})$$

These workers used a modified version of the Hoffmann program which besides doing the m.o. calculation, used this equation to calculate J_{AB} . The results which they obtained are in semi-quantitative agreement with experiment for most cases.

SUMMARY

The extended Hückel theory has been discussed, both the method of calculation and a few examples of typical results. In many cases reasonably accurate calculations of energies have been obtained. However, when one tries to use the wavefunctions to calculate experimental quantities, poor results are usually obtained indicating inaccurate wavefunctions. In the past most workers have attributed this to the inability to estimate the off diagonal elements in the Hamiltonian matrix and much work is being done at present to improve this weakness.

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THE DONOR PROPERTIES OF DIMETHYL CYANAMIDE

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Introduction

References to nitrile complexes with transition metals^{1,2,3,4} are fairly rare in chemical literature although there are many references to complexes formed by cyanide ions ($\text{C}\equiv\text{N}^-$), thiocyanate ions (NCS^-) and the alkyl and aryl isocyanates ($\text{R-N}\equiv\text{C}$).⁵ The properties of nitrile adducts with Lewis bases such as I_2 ⁶, BCl_3 ⁷, and SnCl_4 ⁸ and the hydrogen bonding acid phenol⁹ indicate that the nitriles are poor donors in either a covalent or electrostatic interaction yet they exhibit a fairly large Dq in their transition metal ion complexes. This behavior can be rationalized by invoking π bonding from the metal to a π^* orbital of the $\text{C}\equiv\text{N}$ group. This type of interaction has been investigated by contact shift NMR experiments for $[\text{Ni}(\text{NC}\phi)_6](\text{ClO}_4)_2$.¹

The cyanamides ($\text{R}_2\text{N-C}\equiv\text{N}$) have been exploited even less in inorganic chemistry although their organic chemistry is very extensive. The members of the series are generally quite high boiling liquids which is in accord with their large dipole moments (cyanamide has $\mu = 4.52$ Debye while its nitrile analog $\text{CH}_3\text{C}\equiv\text{N}$ has $\mu = 3.44\text{D}$).

A spectroscopic and semi-empirical LCAO-MO study of the donor properties of dimethyl cyanamide (DMCA) poses an interesting problem for three separate reasons; a) there are at least three possible basic sites in the molecule, b) the nitriles as a class exhibit anomalously large Dq's toward transition metal ions, and c) there is at present some controversy about the structure of DMCA.^{10,11,12}

Klaeboe¹³ has studied the interaction of DMCA with the Lewis acids I_2 and ICl in the infrared and visible regions. Here perturbations on the infrared spectrum of DMCA are not large enough to unequivocally determine the donor site.

Bock¹⁴ has reported several cyanamide nickel carbonyl adducts of unusual structure in which he suggests that the cyanamide is bonding to the $\text{Ni}(0)$ through both the nitrile π cloud and the amino nitrogen lone pair.

Spectral Studies

The infrared and proton NMR spectra of DMCA were investigated in the presence of such Lewis acids as ICl , $(\text{CH}_3)_3\text{SnCl}$, BF_3 , and several phenols. The results are indicative of coordination only through the nitrile nitrogen lone pair. DMCA is a better donor toward these acids than is acetonitrile or benzonitrile as evidenced by larger ΔH 's, K's, spectral shifts and E and C parameters.¹⁵

$\text{Zn}(\text{DMCA})_4(\text{ClO}_4)_2$, $\text{Cu}(\text{DMCA})_4(\text{ClO}_4)_2$ and $\text{Ni}(\text{DMCA})_6(\text{ClO}_4)_2$ were prepared and isolated as extremely hygroscopic solids. The infrared spectra of each complex indicates coordination through the nitrile nitrogen. The NMR contact shift of the DMCA protons and β for the $\text{Ni}(\text{II})$ complex are compatible with this. However, Dq for this complex then seems anomalously low.

EHMO LCAO-MO Results

The results of minimal basis set, valence electron EHMO calculations on cyanamide and DMCA indicate charge distributions which are in accord with the high dipole moment and the increased donor strength of the DMCA nitrile lone pair. The inability of the amino nitrogen lone pair to act as a donor site is indicated.

A comparison of the total energies for several geometries of cyanamide and DMCA indicate the absence of any appreciable barrier to inversion at the amino nitrogen atom while a comparison of the u.v. and visible spectra of DMCA with the calculations favors slightly the C_{2v} planar structure.

The molecular orbitals obtained for DMCA are in agreement with the observed contact shift of the Ni(II) complex only if the $b_2(\pi_z^{**})$ orbital participates in d- π -p π bonding with Ni(II) approximately to the same degree (order of magnitude) as the $b_1(\pi_y^{**})$ orbital which is 0.8 ev lower in energy.

On the basis of the orbital energy scheme predicted in this work an explanation of the bonding of DMCA to Ni(O) in $(Ni(CO)_2DMCA)_2$ is proposed which is at least semantically different from that proposed by Bock.

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MAGNETISM IN THE SOLID STATE—ELECTRON SPIN

RESONANCE AND NEUTRON DIFFRACTION STUDIES

Jerry Atwood

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Introduction

During the past several years our knowledge of the origin of atomic moments and of magnetic order in solids has increased greatly. This increase has been largely stimulated by the development of tools with which the chemist or physicist can study the interactions of individual atoms and ions with each other and with their environments. Two such tools are ESR and neutron diffraction. It is the purpose of this seminar to illustrate the uses of these two methods in the study of transition metal ions in the solid state.

Electron Spin Resonance—Theory^{1,2,3}

Electron spin resonance may be observed when molecules or ions containing one or more unpaired electrons are placed in a magnetic field. In a molecule containing a single unpaired electron, the effect of the magnetic field is to lift the spin degeneracy. Thus the low energy state has the spin magnetic moment aligned with the field while the high energy state has its moment opposed to the field. A transition between the two electron spin energy states can occur upon absorption of a quantum of radiation in the radio frequency or microwave region. The energy of the transition is given by $E = h\nu = g\beta H_0$. The selection rule is $\Delta M_J = \pm 1$. Thus for the single electron case one would expect a single line in the spectrum.

Since ESR is concerned directly with transitions which take place between individual levels, one should consider the perturbations on these levels. Such effects as magnetic exchange between neighboring dipoles, ligand field components of low symmetry, zero field splitting, and nuclear spin place limitations on the use of ESR as well as the interpretation of the spectra.

Magnetic exchange between adjacent magnetic dipoles upsets the arrangement of the ground levels. Even a small amount of magnetic exchange which has very little influence on the magnetic susceptibility is enough to interfere with the interpretation of an ESR experiment. For this reason ESR experiments are usually carried out on paramagnetic substances which have been diluted in a large amount of a diamagnetic substance.

The g value is directly related to the orbital angular momentum, and it is easy to imagine that the orbital motion of the electron will be affected differently whether the orbital motion is about the x, y , or z axes of the crystal system. Thus ligand fields of low symmetry make g anisotropic.

In the absence of any magnetic field, the degeneracy of the M_J levels may be lifted by the presence of a low symmetry ligand field component. If this zero field splitting is large (more than, say, 2 cm^{-1}) the separation of M_J levels differing by unity may be so great that extremely large magnetic fields are necessary to bring the levels close enough for resonance to occur at microwave frequencies. Thus, it may not be possible to observe ESR in complex ions which are distorted.

If a metal ion with unpaired electrons also possesses nuclear spin, the nuclear spin may couple with the electronic spin and give rise to the hyperfine structure of ESR lines. Hyperfine structure may also arise from the spin of the nuclei of the ligand atoms. In this case it is possible to obtain an estimate of the percentage covalent character of the bonds.

It is customary to find the result of an ESR experiment expressed in terms of a spin-Hamiltonian. This spin-Hamiltonian does two things: it provides a means of setting down, in a compact way, the results of many measurements, and it is a starting point for a detailed theoretical discussion of the ion in its environment.

The spin-Hamiltonian is primarily a function of the parameters S' , g , and H , where S' (the "fictitious spin") is a number such that $(2S' + 1)$ is equal to the number of levels in the ground set. A parameter D is used to specify the zero field splitting due to a ligand field of trigonal or tetragonal symmetry. For lower symmetry an additional parameter, E , is used.

The simplest spin-Hamiltonian is for the case considered above where it is only necessary to account for the splitting of a two fold degenerate level by the magnetic field. There is no zero field splitting, and g is isotropic. The spin-Hamiltonian for this system with $S' = 1/2$ is

$$H' = g\beta H S'_z$$

Other spin-Hamiltonians will be considered later in the applications section.

Applications

For the problems given here one should expect ESR to answer the following questions: (1) What magnetic ions are present? (2) What is the symmetry of the ion in the lattice? (3) What is the location of the unpaired electrons?

The first problem under consideration is the detection and study of some unipositive transition metal ions.

The monovalent ions are produced by irradiation of a crystal (NaCl , NaF , MgO , CaO) containing the corresponding divalent impurity with gamma-rays, X-rays, or electrons. Good evidence for the presence of the monovalent ions is obtained from the agreement of the g values for the various configurations.

It is of interest to note that the predicted Jahn-Teller distortion for Ni^{1+} is seen, but for Ni^{1+} in CaO it is in the form of a compressed octahedron. For Ni^{1+} in NaF , the distortion is the more common elongation.

Studies indicate that delocalization of the magnetic electrons of the impurity ions on a nearest neighbor fluorine ion is about 2%.⁶

Next, consider the magnetic properties of spinels.¹⁰

A spinel has the composition AB_2O_4 . The B site is surrounded by an octahedral array of anions, and the A site, by a tetrahedral array. ESR can contribute greatly to the understanding of the distribution of the magnetic ions over the A and B sites, whereas a technique such as X-ray diffraction cannot give unequivocal assignment of oxidation state to the atoms in the different sites.

One of the most studied systems is that of the chromic ion found in the natural ruby spinel (MgAl_2O_4).¹¹ It is found that the spectrum of Cr^{3+} can be explained by a spin-Hamiltonian of the form

$$H_S = g_{||}'\beta H_z S_z + g_{\perp}' (\beta H_x S_x + \beta H_y S_y)$$

with $S' = 1/2$, $g_{||}' = 1.986$, $g_{\perp}' = 3.924$, in which $g_{||}'$ is measured along the body diagonal direction (111). The chromic ion is seen to be surrounded by a distorted octahedral configuration.

Other work of this nature includes the spectra of Mn^{2+} in ZnAl_2O_4 ,¹² and Fe^{3+} in MgAl_2O_4 .¹³

Neutron Diffraction—Theory^{14,15}

The neutron has a magnetic moment of -1.9 in units of the nuclear magneton. It is, therefore, to be expected that a neutron can pass through matter without being disturbed by the presence of electric charges, but that it can be scattered by magnetic dipoles. Indeed, such an interaction was formulated in detail by Halpern and Johnson in 1939,¹⁶ and was experimentally verified shortly thereafter. However, it is only with the advent of large thermal nuclear reactors that beams of neutrons of sufficient intensity to do precise work have come about.

According to the calculations of Halpern and Johnson, the magnetic scattering from paramagnetic ions is described by the differential scattering cross section per unit solid angle,

$$\frac{d\bar{\Phi}_m}{d\Omega} = \frac{2}{3} S(S+1) \left(\frac{e^2 \gamma}{mc^2} \right) f^2$$

S = total spin of the paramagnetic ion. γ = neutron moment in units of nuclear magnetons. f = the amplitude form factor of the ions.

f expresses the decrease in the scattered amplitude resulting from the finite extension of the magnetically active electrons, and is closely similar to the form factor familiar in X-ray work. The form factor variation with angle can be converted to the actual distribution of the magnetically active electrons in the atom by the use of Fourier inversion integral.

For ferromagnetic and antiferromagnetic materials we have

$$\frac{d\bar{\Phi}_m}{d\Omega} = D^2 (\vec{q} \cdot \vec{\lambda})^2 ; D = \left(\frac{e^2 \gamma S}{mc^2} \right) f$$

(where $\vec{\lambda}$ is a unit vector parallel to the polarization of the neutron and \vec{q} is related to a magnetic scattering vector) if we ignore nuclear scattering. If nuclear scattering is included, we have

$$\frac{d\bar{\Phi}_m}{d\Omega} = [C + D(\vec{q} \cdot \vec{\lambda})]^2 = C^2 + 2CD\vec{q} \cdot \vec{\lambda} + D^2 q^2$$

where C is the nuclear scattering amplitude.

When an unpolarized neutron beam is used, we must average the equation for all possible orientations of $\vec{\lambda}$, so that $\vec{q} \cdot \vec{\lambda}$ averages to zero. The differential cross section is then just given by the sum of the nuclear and magnetic contributions:

$$\frac{d\bar{\Phi}_m}{d\Omega} = C^2 + D^2 q^2$$

The magnetic cross section becomes quite sizable and even exceeds the nuclear cross section in many cases.

Applications

In most cases where there is cooperative magnetism, then there will be neutron scattering into coherent Bragg peaks at sharply defined angles of scattering determined by the magnetic unit cell. From a study of these peaks it is possible to determine the magnetic architecture of the solid. On the

other hand, where there is only a random orientation of magnetic moments, in a paramagnetic material, then the portion of the neutron scattering which is magnetic in origin is broadly distributed over a wide angular range, as a general background to the neutron diffraction pattern. Measurements of this background have been used by Atoji^{17,18} to deduce the valency state of certain rare earth carbides.

Another application of interest to chemists is the determination of the radial¹⁹ and spatial^{20,21} distribution of the magnetic electrons. Such work has been done on a limited number of compounds and alloys, and is in good agreement with theoretical calculations.

One of the most significant questions that neutron diffraction can answer has to do with the actual magnetic structure of compounds. MnO was the first such magnetic structure to be studied in detail; by taking powder data at room temperature and at a low temperature Shull and coworkers¹⁹ were able to assign a structure. The magnetic lattice is seen to consist of parallel sheets within which all the Mn²⁺ ions are coupled ferromagnetically but with antiferromagnetic coupling between neighboring sheets. The direction of the magnetic moments in the lattice was determined to be along the cube axes.

Several other structures of interest have been done in recent years,^{22,23} with special attention being devoted to CoO.^{24,25,26}

Summary

The methods of electron spin resonance and neutron diffraction have been successfully applied to certain problems of magnetism in the solid state. There is some overlap between the two methods, but each is seen to have unique areas of application.

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AN APPLICATION OF EXTENDED HUCKEL THEORY TO ELECTRON DENSITY DISTRIBUTION

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August 4, 1966

Introduction

The molecular orbital theory of bonding was introduced approximately thirty years ago by Hund and Mulliken¹, and the simpler form of the theory for conjugated molecules in 1931 by Huckel.² Coulson and Longuet-Higgins later³ put Huckel theory on a "working basis". A recent review⁴ of extended Huckel theory (EHT) summarizes the fundamentals of the theory as well as a few of its applications.

This seminar reports an investigation of the use of extended Huckel theory for electron density prediction. An analysis of orbital exponents, coulomb integrals, and resonance integrals is incorporated in the investigation.

Electron Spin Resonance Coupling Constants

It can be shown⁵ that for a Fermi contact interaction, the hyperfine coupling constant (observed hyperfine splitting) is directly proportional to the unpaired electron density at the nucleus which gives rise to the splitting. Thus

$$a_i = k \{ \psi_{MO}(i) \}^2$$

where a_i is the observed hyperfine splitting for nucleus i , k is a proportionality constant, and $\{ \psi_{MO}(i) \}^2$ is the unpaired electron density at the nucleus (i) in question.

Evaluation of EHT wave functions for unpaired electrons (one configuration) has been carried out at several hydrogen nuclei in planar hydrocarbon radicals in which the unpaired electron exists in an orbital in the plane of the molecule. The effects of orbital exponent variations (Burns⁶, Slater⁷, and Pitzer⁸), of valence state ionization potential (VSIP) variation (Hinze and Jaffe⁹, and Cusachs¹⁰), of off-diagonal element (resonance integral) formulas (Wolfsberg-Helmholz¹¹ and Cusachs¹²), and of VSIP adjustment for charge on the atom (charge adjustment constant = 2.0 for all atoms and charge adjustment determined experimentally for each atom¹⁰) have been carried out (these last three can be termed H-matrix improvements). A set of parameters has been found which yield results consistent with experiment for the phenyl radical (except for the para position), vinyl radical, and cyclohexadienyl radical. These parameters are: Slater orbital exponent on carbon, 1.2 as orbital exponent on hydrogen, Wolfsberg-Helmholz off-diagonal element approximation using proportionality constant = 1.75, Hinze and Jaffe VSIP values, and experimentally determined VSIP adjustments for charge.

Charge Distribution

The set of parameters found most consistent in the calculation of coupling constants was also found best in the prediction of charge distribution, dipole moment calculation (point charge), and orbital population results when compared with other "higher level" calculations (e.g. Pariser-Parr-Pople, ab initio SCF, parametrized SCF) on pyridine, HCN, and H₂CO.

Conclusion

Extended Huckel calculations have been examined from point of view of prediction of electron density in planar molecules. It has been found that these calculations can be used to calculate electron densities if certain improvements are made in the nature of orbital exponent values and the adjustment of H-matrix values for charge on the atoms.

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The Metal-Metal Bond in Metal Atom Clusters and Polynuclear Compounds

Carol Hyatt

August 9, 1966

Introduction

In the last five years, much interest has been directed towards those compounds called "clusters" such as $\text{Nb}_6\text{Cl}_{14} \cdot 7\text{H}_2\text{O}$ and $\text{Cr}_3[\text{Re}_3\text{Cl}_{12}]$, and "polynuclear compounds" such as $[\text{Fe}(\text{CO})_4-\text{Au}(\text{PPh}_3)_2]$ or $[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$, both for their unusual magnetic properties and for their mode of bonding. A cluster compound facilitates study of an isolated, discrete group of nuclei and their interactions upon one another, while a polynuclear compounds promotes speculation on the type of orbitals needed for overlap and their energy requirements.

As of the present, these studies are of a qualitative nature, with some attempt made to correlate spectral, thermochemical, and magnetic properties with the bonding tendencies of the metals themselves.

Although there are many carbonyl compounds which contain metal-metal bonds, this seminar will concentrate on the halide complexes because of their simplicity and neglect of π interactions in bonding theories.

Polynuclear Compounds

J. Lewis, R. S. Nyholm, and colleagues have been responsible for many investigations,¹⁻⁷ and for determining the criteria of a metal-metal bond.^{8,9} In denoting a compound such as $[(\pi\text{C}_5\text{H}_5)\text{Cr}(\text{CO})_3]_2$ (d^5-d^5 configuration) to have an oxidation number of one, they apply the following definition of oxidation state⁸: the formal charge left on an atom when all ligands are removed in their closed shell configuration and any metal-metal bonds are broken homolytically so as to leave an equal number of electrons on each atom.

X-ray data (i.e., the shortness of the metal-metal distance), and magnetic data (i.e., these compounds are diamagnetic and show only a residual temperature dependent magnetism) are by no means absolute criteria. $\text{Mn}_2\text{CO}_{10}$ has a "long" Mn-Mn distance of 2.93 Å,¹⁰ a d^7-d^7 configuration, and is diamagnetic. The $[\text{Ru}_2\text{Cl}_{10}\text{O}]^{4-}$ anion is diamagnetic although each Ru^{IV} has two unpaired electrons. The distance from each Ru to the Bridge O is only 1.8 Å, which is less than the single bond radii of 1.98 Å.¹¹ Bridge interaction is postulated to explain the observed diamagnetism.¹² One only has to mention the anomalous paramagnetism of the copper acetate dimer,¹³ with a Cu-Cu distance of 2.64 Å,¹⁴ to start a debate on whether or not a δ bond really does exist.¹³⁻¹⁷ In addition, spin orbit coupling can quench the magnetic moment of the compound and lead to incorrect conclusions about the number of unpaired electrons. This occurs, for example, in the case of ZrCl_3 , d^1 configuration.*

J. C. Sheldon has attempted to correlate the size of d orbitals and the tendency of the metal to form a metal-metal bond.¹⁸

$$r_{(n-1)d} = \frac{(n^*)^2}{Z^*_{(n-1)d}} \geq 1.4 \text{ \AA}$$

$$R_{M-M} \leq 2r_{(n-1)d} \text{ for a M-M bond}$$

Metals with a "preferred valence state" greater than four, and a r_d/r_s ratio greater than .51, seem to achieve this "valence state" by forming metal-metal bonds, if the metal is in a low oxidation state.¹⁹

Hf(III), Ta(IV), Mo(II), W(V), Te(I), Re(III), and all lower oxidation states of these metals have r_d greater than 1.4, and a r_d/r_s ratio between .73 and .45.

However, the ligand can greatly influence whether a metal-metal bond is formed; substituted phosphines of $Mn_2(CO)_{10}$ were found to be both monomeric and dimeric, according to the nature of the ligand employed.^{1,20}

Some of the heteronuclear compounds prepared include:

$[\pi C_5H_5(CO)_3W-Mo(CO)_3\pi C_5H_5]$,²¹ $[(CO)_5Mn-Re(CO)_5]$,²² $[Ph_3PAu-W\pi C_5H_5(CO)_3]$,¹ $[(C_6H_5)_2CH_3AsCl_2Rh-HgCl]$,²³ $[Fe(CO)_4(HgCl)_2]$,⁷ and $[Mn(CO)_5]_2Fe(CO)_4$.²⁴ L. Dahl et al have investigated some unusual homonuclear Fe compounds, including $Fe_3(CO)_9(Ph-C\equiv C-Ph)$ ²⁵ in which the alkyne bridge distorts the Fe_3 equilateral triangle, and $[C_5H_5FeS]_4$ ^{26,27} in which the Fe_4 moiety is distorted from tetrahedral symmetry. Both Fe atoms are seven coordinate.

Magnus' Green Salt $[Pt(NH_3)_4][PtCl_4]$

S. Yamada²⁶ first noticed that the circular dichroism of the compound was "abnormal", i.e. $\frac{\alpha_{\perp}}{\alpha_{\parallel}} = 1.25$ where the electric vector

of the polarized light is parallel or perpendicular to the square plane MX_4 . α_{\parallel} is usually more intense in "normal" MX_4 complexes.

J. R. Miller²⁹ synthesized 10 double complex salts of Cu, Pd, and Pt isomorphous to Magnus' green salt, and only the compounds containing Pt in both anion and cation were colored and showed the abnormal dichroism. Since the compounds do not contain a chlorine bridge, as in $Pt(NH_3)_2Br_2 \cdot Pt(NH_3)_2Br_4$,³⁰ the "abnormal" dichroism seems to indicate metal-metal interaction. Note that the structure alone does not imply this interaction, since all 10 compounds are isomorphous.

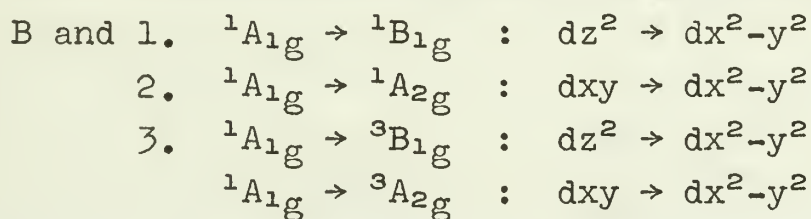
To investigate Rundle's theory³¹ that the metal promotes an anti-bonding a_1^* electron from the $(4s + 3d_{z^2})$ orbital to a non-bonding a_{2u} (P_z) orbital, and uses this electron in forming the metal bond, Miller measured the reflectance spectra of the salts.³²

For example:

	$\bar{\nu}$	Color	$\sim 4 \times 10^{-3}$	$\sqrt[3]{\bar{\nu}}$	$\sqrt[2]{\bar{\nu}}$	$\sqrt[1]{\bar{\nu}}$
$[\text{Pden}_2][\text{PtCl}_4]$	3.40	Pink	--	19.3	--	27.1
$[\text{Pt}(\text{NH}_3)_4][\text{PtCl}_4]$	3.23	Green	6.4	16.4	25.0	29.0

$\sqrt[3]{\bar{\nu}}$ appeared to be very sensitive to changes in interionic distances in the region of 3.25 Å for the chloroplatinates and shifted strongly as one moved down the series. Platinum cations caused considerably lower frequencies than the palladium cations, when the same ligand was involved.

The assignments are as follows: (D_{4h} symmetry)



Bands 1 and 3 would therefore be more affected by the nature of the cation in the series of chloroplatinates. This assignment disagrees with that of Ballhausen and Gray.³³

The strong, broad absorption at 6000 cm^{-1} is assigned in accordance with Rundle's theory of "crystal orbitals", p_z and d_{z^2} , extending along the crystal c axis. This crystal interaction results in four energy bands, and the allowed transition is from an upper, filled d band to a lower, empty p band.

Further experiments are needed to test the validity of this reasoning and of the band assignments.

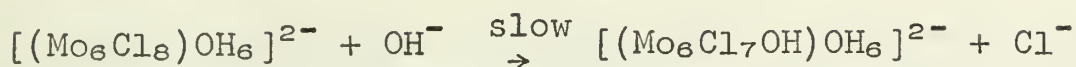
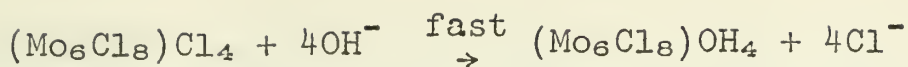
Metal Halide Compounds

One can conveniently divide these halide complexes into three types:

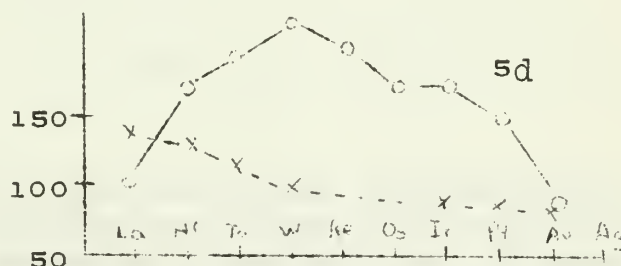
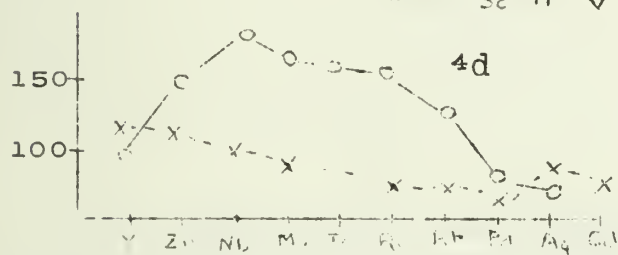
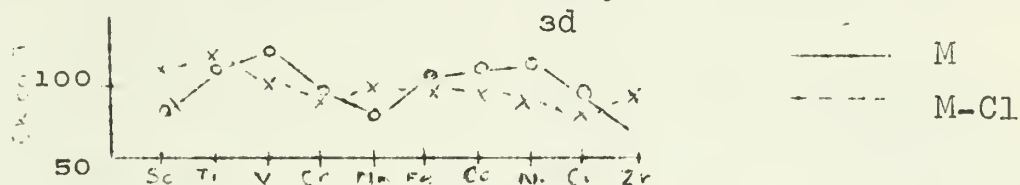
- hexanuclear octahedral clusters represented by $[\text{M}_6\text{X}_{12}]^{2+}$ and $[\text{M}_6\text{X}_8]^{4+}$
- triangular clusters such as Nb_3Cl_8 ,³⁴ $[\text{Re}_3\text{Cl}_{12}]^{3-}$ ³⁵ and $[\text{Re}_3\text{Cl}_{11}]^{2-}$ ³⁶
- binuclear complexes such as $[\text{W}_2\text{Cl}_9]^{3-}$ ³⁷ and $[\text{Re}_2\text{Cl}_8]^{2-}$.^{38,39}

The first group includes the fluorides, chlorides, and iodides of Mo, W, Nb, Ta, many of which have been synthesized by H. Schäfer and H. G. Schnering.⁴⁰

The clusters may contain "inner" and "outer" halide groups represented by $[\text{M}_6\text{X}_{12}]\text{X}_2^0$, $[\text{M}_6\text{X}_8]\text{X}_4^0$, $[\text{M}_3\text{X}_{12}]\text{X}_3^0$, $[\text{M}_2\text{X}_8]\text{X}_2^0$. J. C. Sheldon⁴¹ has shown that OH^- attack on the hexamolybdate II compound is $\text{S}_{\text{N}2}$, implying that the $[\text{Mo}_6\text{Cl}_8]^{4+}$ group is too rigid to be distorted into an activated complex.



If one graphs the heat of sublimation of the free metal and the heat of formation of the metal-chloride bond for the elements of the first, second, and third transition series, one notices that a maximum occurs at Nb and Mo in the second series, and Ta, W, Re in the third. These are the elements most likely to form M_6 clusters.⁴²



One may also compare the metal-metal distance of the free element with the distance in a compound where a metal-metal bond is suspected. However, NbI_4 , a d^1-d^1 compound, has a Nb-Nb distance of 3.31 Å and is diamagnetic;⁴³ the single bond metal-metal radius is 2.68 Å.¹¹ A new criterion has been proposed,⁴² namely the ratio $\Delta d/\bar{d}$, where \bar{d} is equal to one-half the metal-metal distance plus the neighboring metal-metal distance $1/2[d_1(\text{M-M}) + d_2(\text{M-M})]$, and $\Delta d = (d_1 - \bar{d})$.

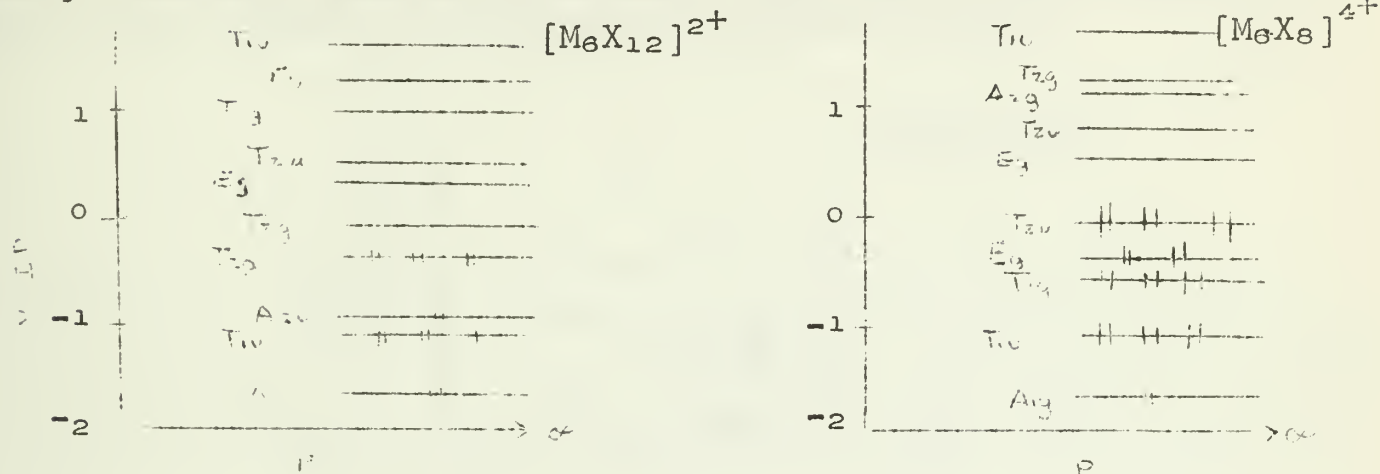
Bonding in Metal Atom Clusters

A valid MO theory should be able to explain the metal-metal bonding in all three types of clusters. One can conceive of polycentric orbitals, rather than two-centered bonds for these compounds. Cotton and Haas⁴⁴ have based their MO description on the model of the MX_4 group. In the hexa-atomic species, the angle between the metal-halogen bond and the C_4 axis of the octahedron is approximately 81° ; the trinuclear Re group can be considered three distorted MX_4 groups; in $[\text{Re}_2\text{Cl}_8]^{2-}$, the two MX_4 planes are only slightly distorted, at an angle of 87° .

In valence bond terminology, the metal uses dsp^2 hybridization: dx^2-y^2 or dxy , an s, px and py orbitals for bonding to the four halogens. This leaves the pz and the four other d orbitals; assume that the pz and dz^2 do not hybridize.

The M₆ group

For each metal atom, let each local z axis point toward the center of the octahedron. For $[M_6X_8]^{4+}$, dxy is not used; for $[M_6X_{12}]^{2+}$ the dx^2-y^2 is not used. The following are the MO schemes:



For $[Nb_6Cl_{12}]^{2+}$ and $[Ta_6Cl_{12}]^{2+}$, the free atom configuration is d^3s^2 , leaving 16 electrons for the metal-metal bond. Using Cotton's scheme, this fits in well with the observed diamagnetism. However, since the publication of that paper, Mo_6Cl_{12} and W_6Cl_{12} have been prepared;⁹ configuration, d^5s^1 , leaving 24 electrons for the metal-metal bond, if all of the chlorines are "inner sphere" chlorines. This would imply two electrons in the E_g levels. The magnetic susceptibility of these new compounds have not yet been reported. W_6Br_{16} , however, is reported by the same authors to contain $[W_6Br_8]^{6+}$ and a linear $[Br_4]^{2-}$ group. The stoichiometry of the compound by no means indicates the cluster it contains.

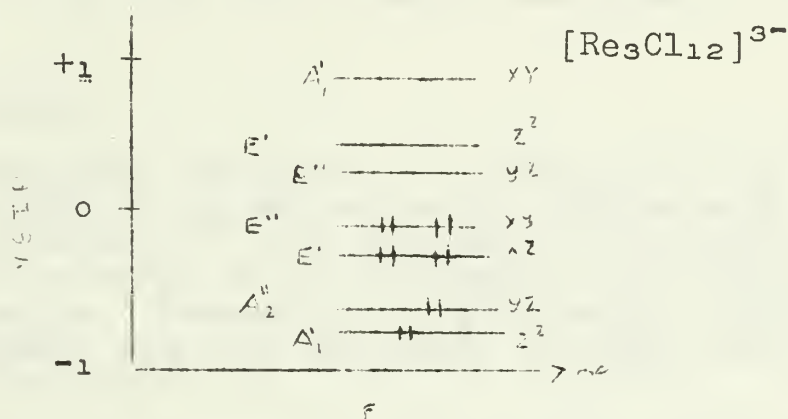
For the $[M_6X_8]^{4+}$ system, where $M = Mo, W, (d^5s^1)$, 24 electrons are left for the metal-metal bond. Again, the MO scheme is consistent with the observed diamagnetism.

Leon Crossman⁴⁵ has proposed a different MO scheme, which designates the basis set of orbitals as those directed to a vertex, or over the face, or over the edges of the octahedron. The scheme is not as simple as Cotton's, and the resulting bonding energy orbitals are the following: for $[M_6X_{12}]^{2+}$, $A_{1g}, A_{2u}, F_{2g}, F_{1u}$; for $[M_6X_8]^{4+}$, $A_{1g}, F_{2g}, F_{2u}, E_g, F_{2u}$.

The M₃ group

$Cs_3[ReCl_4]_3$ contains the tri-rhenium cluster $[Re_3Cl_{12}]^{3-}$. From the crystal structure, one immediately notices that, unlike the M_6 cluster, there are two types of chlorines. The Re-Cl "inplane" distance is 2.52 Å, while the Re-Cl bridge and axial distances are 2.39 Å and 2.36 Å respectively. The three bridge chlorines are not subject to exchange,⁴⁶ suggesting that the stable moiety is actually $[Re_3X_3]^{6+}$.

Two interesting derivatives of the Re_3 cluster are $\text{Re}_3\text{Br}_3(\text{AsO}_4)_2(\text{DMSO})_3$ ⁴⁷ and $\text{Re}_3(\text{Se-}\emptyset)_3(\text{CO})_9$.⁴⁸ From IR evidence, the first is thought to contain two AsO_4 groups, each O_3 plane parallel to the $[\text{Re}_3\text{Br}_3]^{6+}$ plane; the second contains selenium, rather than halogen, bridges. Continuing Cotton's approach to the bonding in terms of MX_4 units, we obtain the following MO scheme:

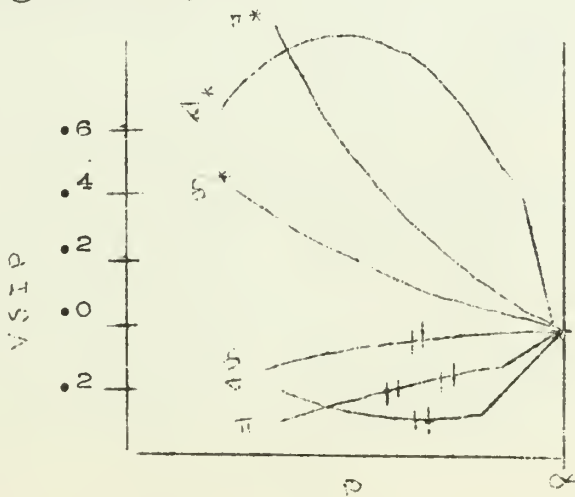


The three rhenium atoms (ground state configuration of d^5s^2) contribute 12 electrons to the metal-metal bond, and the scheme agrees with the observed diamagnetism. R. Colton and R. L. Martin⁴⁹ have prepared the rhenium IV chloride, $\text{Re}_3\text{Cl}_{12}$ which exhibits a magnetic susceptibility equivalent to one free electron ($\mu = 1.02 - 1.13$ from 304°K to 87°K). The above MO scheme also agrees with this data.

$[\text{Re}_2\text{Cl}_8]^{2-}$

The two most unusual aspects of this compound are the short Re-Re distance of 2.24 Å and the fact that the two chlorine planes are eclipsed, rather than staggered, despite the short distance between them.³⁹

According to Cotton's MO scheme,⁵⁰ one uses dsp^2 orbitals for sigma bonding to the four chlorines; the d orbital chosen is the x^2-y^2 . Considering the Re-Re bond, the dz^2 and p_z have σ symmetry, the dxz and dyz , π symmetry, and the dxy has δ symmetry. Each Re (d^5s^2) contributes four electrons to the metal-metal bond, resulting in the ground state molecular orbital configuration $\sigma^2\pi^4\delta^2$, a closed shell configuration.



Cotton argues that the δ bond necessitates that the chlorines be eclipsed, since the staggered configuration would negate the possibility of this fourth bond. The short distance also seems indicative of some type of "special" bonding; 12 electrons per three metal pairs makes the bond order equal approximately to 2. Cotton's assignment of the electronic spectra including a $\delta \rightarrow \delta^*$ transition, is "most tentative", as the author admits. Currently, neither an argument against the δ bond, nor a better assignment of the spectra has appeared.

Platinum-Tin Clusters

Although a compound formulated as $[\text{PtSn}_4\text{Cl}_4]^{4+}$ can be found in the literature in 1955,⁵¹ it was not until 1965 when R. D. Cramer did the crystal structure.⁵² The compound is correctly formulated as $\text{L}_3\text{Pt}[(\text{SnCl}_3)_5]$ and contains Pt in the center of a trigonal bi-pyramid formed by the Sn atoms. Recently, a Pt_3Sn_2 metal cluster, with the Sn atoms at the apexes has been reported, but only IR evidence is given for the structure.⁵³

Only preliminary investigations have been carried on relating to the reactivity,⁵⁴ kinetics,⁵⁵ or Mossbauer spectra⁵⁶ of metal-tin compounds.

Novel Methods of Approach to the metal-metal bond

For those interested in Raman spectra and its ambiguities, see reference 57.

If you enjoyed Hess' Law of Constant Heat Summation, consult Cotton's thermochemical calculations in reference 58.

A more practical approach is found in R. B. King's⁵⁹ article on the mass spectra of some polynuclear metal carbonyls.

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Fred K. Ross

October 13, 1966

INTRODUCTION

Mössbauer spectroscopy is rapidly emerging as a useful tool for elucidating structure and investigating bonding in inorganic materials. It is intended that this seminar might serve as a starting point for an understanding of the "Mössbauer Effect" and as a guideline for probing the validity of applications to inorganic chemistry.

HISTORICAL

The concept of nuclear resonance fluorescence, the general resonance phenomenon of which the Mössbauer Effect is a specialized case, by no means originated with the studies of Mössbauer. Resonance in atomic systems had been demonstrated by R. W. Wood (1) early in the century and the possibility of observing its parallel in nuclear systems was recognized soon afterward. The search for nuclear resonance was begun by Kuhn (2) in 1929. However, even though the problems in atomic and nuclear resonance seem very similar, there exist marked differences which render nuclear experiments much more difficult. The major factors contributing to this difficulty are:

- 1) Recoil Energy - The kinetic energy imparted to the nucleus by the emitted photon as required by the conservation of momentum.

$$R = E\gamma^2/2mc^2 \quad \begin{array}{l} R = 10^{-11} \text{ ev (optical transitions)} \\ = 10^{-5} \text{ ev (nuclear transitions)} \\ \text{with } A = 100 \text{ AMU.} \end{array}$$

- 2) Line Width of Emitted Radiation - The natural line width Γ for a state of mean lifetime τ is given by the Heisenberg uncertainty relation $\tau \cdot \Gamma = \hbar$.

By replacing the mean lifetime τ by the equivalence $\tau = \frac{1/2}{0.693}$

where $\tau_{1/2}$ is the half-life of the state, one finds $\Gamma = \frac{0.693\hbar}{\tau_{1/2}}$

For the value $\tau_{1/2} = 10^{-7}$ sec. (a reasonable value for both electronic and nuclear transitions) the linewidth is found to be 4.6×10^{-9} ev.

Since this value is considerably greater than the recoil energy for optical transitions, overlap of emission and absorption lines (on a linear energy scale) is assured. However, it is obvious that no overlap occurs for the nuclear case. Some experiments in nuclear resonance were successfully carried out by attaching the emitter to an ultracentrifuge. At velocities of $\sim 8 \times 10^4$ cm/sec, it was found possible to exactly compensate for recoil in both the source and the absorber for Au^{198} (3,4).

- 3) Thermal Broadening - The energy added by virtue of a moving source as mentioned above is called the Doppler energy. For a vibrating nucleus, this leads to additional broadening of the emission and absorption lines. The magnitude of the Doppler broadening is given by the approximation

$$\bar{D} = 2(\bar{\epsilon}R)^{1/2}$$

where $\bar{\epsilon}$ = average kinetic energy of the nuclei involved.

For optical radiation, the recoil energy R is small compared to the Doppler broadening. For gamma rays, the recoil energy is at least comparable to and usually larger than the Doppler broadening.

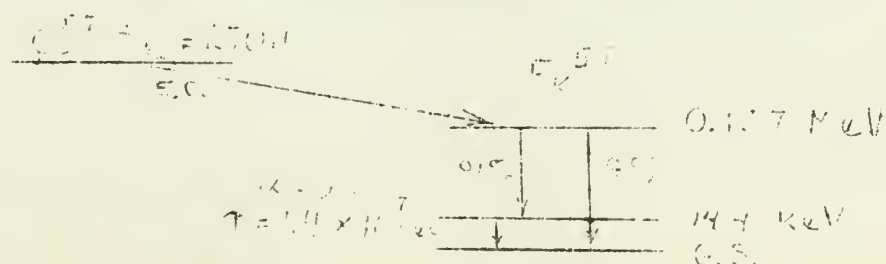
THE EXPERIMENT OF MÖSSBAUER (5,6,7)

In 1957, Rudolph Mössbauer, a graduate student at the Max Plank Institute for Medical Research in Heidelberg, was studying the 129 keV transition of Ir^{191} . For this transition, the free recoil energy R is 0.05 eV and the Doppler broadening at room temperature is about 0.1 eV. Thus, at room temperature the emission and absorption spectra overlap considerably. In studying the temperature dependence of this overlap, Mössbauer cooled the source to minimize the Doppler broadening which in turn minimizes the degree of overlap and should allow a "background" count rate to be determined. Instead of a minimum resonance condition, he found a marked increase in absorption. Mössbauer quickly recognized that, at low temperatures, the nucleus becomes tightly bound in the lattice, the mass of the recoiling system becomes that of the entire lattice (hence, $R \rightarrow 0$) and a fraction of the emitted gamma rays are unshifted and display a width equal to the natural line width.

Thus, the Mössbauer Effect is that specific case of nuclear resonance fluorescence in which the recoil of the emitting and absorbing nuclei is restricted by rigid bonding in a crystal lattice. The energy of the gamma ray emitted by the source in such a lattice at a sufficiently low temperature (to minimize Doppler broadening) now coincides exactly with that of the absorber (also at low temperature). Since the natural line width of the transition is so narrow, the Mössbauer effect is very sensitive to slight changes in energy for the transition in the absorber as compared to that of the emitter. This sensitivity makes possible the study of extremely small perturbations on the nuclear energy levels and this is the field of Mössbauer spectroscopy.

OTHER FACTORS OF INFLUENCE

The excited state (of the emitter) is usually obtained for Mössbauer spectroscopy as the product of a beta decay or electron capture in the "parent nucleus". For example, consider the decay process of Co^{57} :



Several requirements must be met by such a decay scheme to allow for practical observation of the Mössbauer spectrum.

- a) The transition from an excited state should have an energy of between several and several hundred keV and must be of great enough intensity to provide adequate detection (intensity losses occur through branching decay modes, competition of internal conversion, etc.).
- b) The nucleus to be excited must have an adequate cross-section for gamma absorption.
- c) The parent isotope Co^{57} in this case) must be conveniently accessible.

Fortunately, the factors above and other more subtle ones not mentioned have been considered by numerous investigators and tables of convenient nuclei for Mössbauer spectroscopy are given in several of the review sources listed in the bibliography.

PERTURBATIONS OF THE NUCLEAR ENERGY LEVELS WHICH ARE OF CHEMICAL INTEREST

A. ISOMER SHIFT - The s electrons of chemically bonded atoms have a finite density at the nucleus which depends upon the electronic distribution in bonding. This gives rise to an interaction which serves to change the energy of the nuclear transition from the ground to the excited state. For this reason, the energy of the gamma ray emitted by a nucleus in a nucleus in a given chemical environment may no longer overlap with the energy required to provide nuclear excitation in the absorber even though the recoil has been quenched by bonding. Additional energy must be added to or subtracted from the emitted gamma ray to again establish the resonance condition. This is most conveniently done by adding (or subtracting) energy by moving the emitter toward (or away from) the absorber. This corresponds to adding an energy equal to $E' = m v^2$ and is the same effect as that observed in Doppler broadening.

By choosing a convenient standard, a relative table of such "added energies" or isomer shifts can be established. This shift is given by

$$\text{I.S.} = \frac{2\pi Z_c^2}{5} (R_{\text{ex}}^2 - R_{\text{gd}}^2) \left\{ \left| \psi(0) \right|_{\text{ABS.}}^2 - \left| \psi(0) \right|_{\text{source}}^2 \right\}$$

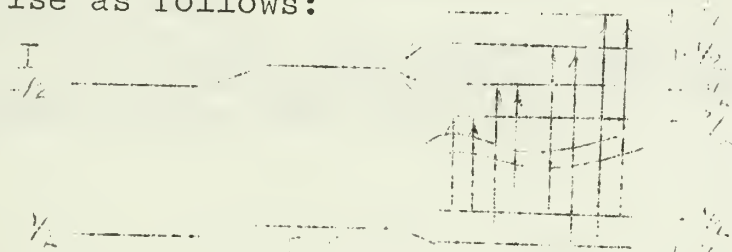
where $\left| \psi(0) \right|_{\text{ABS.}}^2$ and $\left| \psi(0) \right|_{\text{source}}^2$ are the electronic charge densities at the nucleus for the absorber and the source respectively. R_{ex} and R_{gd} are the nuclear radii of the excited and ground states.

B. QUADRUPOLE SPLITTING - The presence of a nuclear quadrupole presents the possibility of splitting of the spectral line observed for a transition. Thus, for Fe^{57} which has a quadrupolar excited state ($I=3/2$) the following transitions are possible:



The spectrum of Fe^{57} in biferrocenyl at 20°K (8) shows this quadrupole splitting. At the present time, the only entirely safe applications of quadrupole splitting are those of distinguishing symmetry or asymmetry in crystal fields.

C. MAGNETIC HYPERFINE INTERACTIONS - Interactions of nuclear ground and excited states with the magnetic moment arising from the mechanical nuclear spin give rise to magnetic hyperfine interactions in the Mössbauer spectrum. The interaction splits the nuclear state into $2I+1$ levels. The magnetic hyperfine interactions in the spectrum of Fe^{57} arise as follows:



The six-line spectrum has been observed and persists until temperatures in the neighborhood of the curie point of iron (769°K).

APPLICATIONS

More applications of Mössbauer spectroscopy have been applied to iron and tin than to all other nuclei combined. In addition to the areas of electron density in bonding (isomer shift), geometry (quadrupole splitting) and determination of nuclear magnetic fields (hyperfine interaction), countless other applications exist and more are being found. These include temperature shifts (9,10) and line broadening studies (11,12) which facilitate investigations of crystal bonding effects and lattice parameters.

Extensive surveys of the literature are found in each of the general references listed. These, combined with the Nuclear Science Abstract index, provide an excellent means of surveying all chemical applications developed to date.

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NUCLEAR MAGNETIC RESONANCE PSEUDOCONTACT SHIFTS

R. E. Cramer

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INTRODUCTION

The effects of unpaired electrons on the nuclear magnetic resonance of molecules were noticed early by Bloembergen (1), who observed that the line widths of various resonances were increased by adding paramagnetic ions to a solution of molecules containing the resonating species. Bloembergen (2) also noticed that the addition of paramagnetic ions caused a shift of the NMR lines. Later, McConnell (3) realized that these isotropic NMR shifts could have two origins, the Fermi contact shift (4), or a pseudocontact shift.

THEORY

Originally, it was believed that it would be impossible to observe NMR spectra of paramagnetic compounds because the field of the unpaired electron greatly decreases the spin-lattice relaxation time of a resonating nucleus. The lines are thus extremely broad. However, if the electron is relaxed rapidly, its field averages to zero, and the proton relaxation time is left unaltered, resulting in sharp NMR lines (5). Hence, the condition for observing NMR of paramagnetic molecules is that $1/T_1 \gg A$ or $1/T_{1e} \gg A$ or both, where T_1 is the electron spin lattice relaxation time, T_{1e} is the characteristic electronic exchange time, and A is the hyperfine splitting constant of the proton by the electron (6). If either of these two conditions are satisfied, then an isotropic NMR shift can result through two independent mechanisms. The first is the "contact" interaction, which is transmitted through bonds and arises because an electron in an S orbital has a finite probability of existing at the nucleus (4). The second is the "pseudocontact" or dipolar effect which is transmitted through space and arises as a result of anisotropy of the g tensor of the metal ion (7). In general, a transition metal can be expected to have an anisotropic g tensor whenever the site symmetry is less than cubic.

McConnell (7) has derived the equations for the pseudocontact shift assuming that $T_1 > T_{1e}$, obtaining

$$\Delta H_i/H = -B^2 S(S+1)/27kT (3\cos^2\theta_i - 1)/r_i^3 (g_{11} + 2g_1)(g_{11} - g_1) \quad (1)$$

for the pseudocontact shift for species in solution. Here $\Delta H_i/H$ is the fractional isotropic dipolar shift of the i^{th} proton, r_i is the radius vector from the metal ion to proton i , θ_i is the angle between the highest fold symmetry axis of the molecule and the radius vector of the proton i , B is the Bohr magneton, S is the total spin quantum number, and g_{11} and g_1 are the components of the g tensor parallel to and perpendicular to the highest fold symmetry axis. This equation as originally reported contained a sign error which has since been corrected by La Mar (8). McConnell also gave the equation for the pseudocontact shift in the solid as

$$\Delta H_i/H = -B^2 S(S+1)/9kT (3\cos^2\theta_i - 1)/r_i^3 (g_{11} + g_1)(g_{11} - g_1) \quad (2)$$

We can easily see that the contribution to the isotropic shift from the pseudocontact shift is different in the solid than in solution. This method has been used by McConnell and Holm (9) to suggest that in nickelocene a pseudocontact mechanism may be operating. Usually, however, the line widths in the solid are too great to permit this type of analysis.

La Mar (8) has also developed equations for the C_{2v} case, and for the case where $T_{1e} > T_1$.

EXPERIMENTAL

The most common method used to deal with the pseudocontact shift experimentally is to ignore it. Thus, Eaton (10) et. al. argue away a pseudocontact shift in the bis(aminotroponeimine) nickel(II) complexes by assuming that the nitrogen donors are arranged in a tetrahedral manner around the nickel ion. Holm (11) and his co-workers used the same assumption in ignoring pseudocontact shifts in the bis(salicylaldimine) nickel(II) complexes, in spite of the fact that X-ray studies show that there is significant distortion from idealized C_{2v} symmetry. Many other similar cases could be cited.

The first paper in which a real effort was made to separate out the pseudocontact shift concerned a study of pyridine adducts of Ni(II) and Co(II) acetylacetonates by Happe and Ward (12). As part of this study, they made the 4-phenyl pyridine adducts and assumed that any observed shift at the para phenyl protons would have to be due to a pseudocontact term. Using the geometric ratios for the para phenyl proton, and any other proton in the system, they were able to evaluate the maximum possible pseudocontact contribution at any position. The good agreement which they obtained in the ratios of contact shift values for the same ligand coordinated to Ni(AA)₂ and Co(AA)₂ is good evidence that their original assumption was valid.

Horrocks, Taylor and La Mar (15) also studied the isotropic shifts of triarylphosphine and isonitrile ligands coordinated to Ni(II) and Co(II) acetylacetonates. They were able to separate the pseudocontact shift by making two assumptions. Firstly, they assumed that there was no pseudocontact term in the Ni(II) adducts. Secondly, they assumed that the distribution of unpaired electron density should be the same in any ligand whether coordinated to Ni(AA)₂ or Co(AA)₂. The various proton contact shift ratios of the Co(AA)₂·ligand₂ complexes were made to agree with the equivalent ratios for the Ni(AA)₂·ligand₂ complexes by subtracting a pseudocontact term from the observed resonances of the Co compound. The resulting ratios for the Co and Ni compounds agreed well. These pseudocontact shifts were also found to greatly improve the agreement of Q_{CH_3} (vide infra) values for the same ligand on Co(AA)₂ and Ni(AA)₂.

Horrocks and La Mar (13,16) have also studied the isotropic shifts of the bis(triarylphosphine) complexes of Co(II) and Ni(II) dihalides. The equation for the pseudocontact term in C_{2v} symmetry is given as

$$\Delta H_1/H = -B^2S(S+1)/27kT(g_1+g_2+g_3)[(g_1-1/2g_2-1/2g_3)(3\cos^2\theta_1-1) - 3/2(g_2-g_3)(\sin^2\theta_1\cos 2\phi_1)](1/R_1)$$

The pseudocontact shift in the Ni(II) complex was assumed to be zero since the ratios of the observed shifts in the phenyl rings were the same as those observed by Eaton (10) for the phenyl rings in N,N di-phenylaminotroponeiminate Ni(II). A pseudocontact shift was postulated for Co(II) complexes since the ratios of the protons of the phenyl rings were vastly different from those observed by Eaton. A pseudocontact shift for the Co(II) complexes was estimated by calculating the two geometric ratios in Eq. (3) and then fitting the ratios of the phenyl proton shifts of the Co(II) complex to those of the Ni(II) complex. As a check a calculation of Q_{CH_3} was made from the equation

$$A_i = Q_{CH_3} P_i \quad (4)$$

where A_i is the contact shift, Q_{CH_3} is a constant, and P_i is the electron spin density at the i^{th} carbon. It was found that the calculated pseudocontact shifts greatly improved the agreement of Q_{CH_3} values. Also of interest is the fact that the pseudocontact shift is larger in the iodides than in the bromides. This is to be expected, since the difference in position in the spectrochemical of ϕ_3P and I^- is greater than the difference between ϕ_3P and Br^- . Thus the iodide would have a larger C_{2V} distortion, and hence a larger g anisotropy causing a larger pseudocontact shift.

Kluiber and Horrocks have used the same method to separate out the pseudocontact shifts of complexes of Ni(AA)₂ and Co(AA)₂ with quinoline 1-oxide (16), isoquinoline 2-oxide and pyridine N-oxide (17). It was found that in these compounds in order to get the geometric ratio to agree with the calculated pseudocontact shifts, an M-O-N angle of 114°-130° must be assumed, with the best fit generally at 115°.

La Mar and Horrocks (18,19,20) have obtained the best evidence to date for a pseudocontact shift by observing isotropic shifts for the protons of tetrabutylammonium cations which are ion paired in solution with anionic transition metal complexes. Studies on the tetrabutylammonium triphenylphosphine metal triiodide systems, where the metal is Co(II) or Ni(II), enabled La Mar to obtain more valid estimates for the pseudocontact shifts of the phenyl protons (18) and to calculate the interionic distance in the ion pair (19). In a similar study of tetrabutylammonium tris(acetylacetonato) Co(II) and Ni(II), Horrocks (20) et. al. found that the pseudocontact shifts for the 3-hydrogen of the chelate may be as great as 1200 cps. Results for the pseudocontact shift for the chelate protons calculated from the observed shift for the butyl protons, and calculated by forcing the ratio of the shifts of CH₃ to H to be the same in Co(II) and in Ni(II) complexes agreed to within 20%.

Rettig and Drago (21) have used the apparent absence of a pseudocontact interaction at the chloroform proton to deduce the structure of chloroform adducts of tetrabutylammonium triphenylphosphine Co(II) and Ni(II) triiodides. The geometry necessary for the absence of a pseudocontact shift requires that the chloroform hydrogen bond to either the iodine atoms or to the phenyl rings.

CONCLUSION

Pseudocontact shifts have been observed for a variety of transition metal complexes. It is evident that care must be taken in interpreting contact shift data whenever a pseudocontact shift may be present. It is also apparent that a pseudocontact shift will appear whenever the symmetry of the complex is less than cubic, even when this distortion from cubic symmetry is not great.

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BONDING AND STRUCTURE IN METAL NITROSYLS

Larry M. Ludwick

November 3, 1966

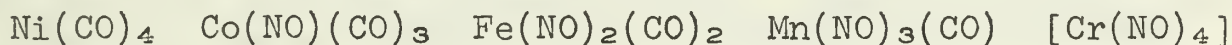
INTRODUCTION

Nitric oxide as a coordinating ligand appears relatively simple while in truth it offers some of the most perplexing problems in complex chemistry. This seminar will deal principally with the cyano-nitrosyls where the most systematic and detailed work has been done.

The electronic structure of the nitric oxide molecule accounts for its many-sided behavior as a coordinating ligand. According to simple molecular orbital considerations the neutral molecule possesses one electron in an antibonding orbital. This electron is lost with relative ease (the ionization potential for NO is much lower than that of N₂ or CO) to form the nitrosonium ion (NO⁺) which is isoelectronic with N₂, CN⁻ and CO. The increase in the strength of the NO bond resulting from the loss of this antibonding electron is shown by the increase in the NO stretching frequency from 1888 cm.⁻¹ in free NO gas to 2200-2300 cm.⁻¹ in nitrosonium salts. Consequently NO⁺, NO and NO⁻ species are all possible in nitric oxide complexes.

TYPES OF COORDINATION

(1). NO⁺ This type of coordination is seen to involve the transfer of the odd electron from NO to the metal ion followed by lone pair donation from NO⁺. Using this three electron scheme, much of the general chemistry of the nitric oxide compounds can be rationalized. For example, the pseudo nickel carbonyl series



is understandable. The final member is unknown but the first members all obey the inert gas rule. The reduction in the atomic number of the central metal atom is compensated for by the substitution of NO (three electron donation) for CO (two electron donation).

(2). NO This is simply the donation of the lone pair on the nitrogen and the retention of the odd electron by the NO group. All complexes involving this type would be paramagnetic due to the unpaired electron.

(3). NO⁻ This involves the transfer of an electron from the metal to NO, forming NO⁻ which then acts as a normal ligand. The existence of this type of coordination has recently been questioned (1,2). Many compounds long thought to contain the NO⁻ group now are often better formulated as containing the dimeric hyponitrite ion N₂O₂²⁻.

(4). NO Bridging This is postulated by analogy to the bridging by CO groups which occurs in many polynuclear carbonyls.

An interesting illustration of the problem involved is found in the nitrosyl, Fe(NO)₄. Sidgwick (3), reasoning from the rare gas rule, postulated a nitrosonium ion [NO⁺][Fe(NO)₃]. Later, Griffith, Lewis, and Wilkinson (4) following infrared data suggested both NO⁺ and NO⁻ in

It is well known that the most important factor in the development of a disease is the environment. This is especially true in the case of the common cold, which is caused by a virus that is spread by contact with an infected person. The virus enters the body through the nose or mouth and then travels to the throat and lungs.

The environment also plays a role in the development of other diseases. For example, a person who lives in a crowded, unsanitary environment is more likely to develop a disease than a person who lives in a clean, well-ventilated environment. This is because the crowded environment provides a favorable medium for the growth and spread of disease-causing organisms. In addition, a person who is exposed to cold and wet weather is more likely to develop a cold than a person who is kept warm and dry.

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$[(\text{NO}^+)_3\text{Fe}(\text{NO}^-)]$ analogous to $[(\text{NO})_3\text{FeCl}_3]$. The most recent suggestion (2) is that the molecule is a dimer involving the hyponitrite ion $(\text{NO}^+)_3\text{Fe}-\text{ON}=\text{NO}-\text{Fe}(\text{NO}^+)_3$. Such complications occur with great frequency in nitrosyl chemistry and it is important to realize that any one formal description is no doubt a highly inaccurate description of reality. The available data suggest that metal-nitrosyl complexes should be considered as molecular species with electrons delocalized to different extents rather than containing charged or uncharged ligands.

EXPERIMENTAL METHODS

Lewis, Irving and Wilkinson (5,6) have proposed that frequencies in the range $1045-1200 \text{ cm}^{-1}$ be attributed to the NO^- group, while those in the range $1575-1930 \text{ cm}^{-1}$ be attributed to the coordination of NO^+ . This assignment has been challenged recently by Gans (7) who feels that frequencies in the range $1500-1700 \text{ cm}^{-1}$ should be assigned to NO^- while frequencies in the range $1700-1900 \text{ cm}^{-1}$ should be treated individually on their own merits. The assignment based on the work by Lewis and coworkers is still the most successful despite several ambiguities.

The chemical properties of a complex can often be used to argue for the presence of a certain type of coordination in nitrosyls. This mainly concerns a consideration of the oxidation state of the metal, its geometry and its stereochemistry. For example, in $\text{PtCl}_5\text{NO}^{2-}$ the infrared (1711 cm^{-1}) indicates the presence of NO^+ and Pt(II) . However, the stereochemistry of the complex is more compatible with a Pt(IV) complex of NO^- . In this respect, Gans' infrared assignment would not be in conflict with the presence of NO^- . The stability of the complex can often be used as evidence when considering monomer-dimer formulations.

The magnetic behavior of compounds can be taken as an indication of the type of coordination. Consistent with the frequency of NO^+ , the majority of the nitrosyls are diamagnetic. Although diamagnetism rules out the presence of neutral NO , in general the information obtained in this manner is less definitive than is desired.

An accurate description of the molecule in terms of bond angles and bond distances should lead to fairly definite conclusions as to the nature of the NO coordination. However, here the lack of experimental results limits this approach. In the case of $[\text{Co}(\text{NH}_3)_5\text{NO}]\text{Cl}_2$ (black form) (8), the authors say that they are unable to tell with certainty whether the nitrogen or the oxygen is bound to the metal. The question can usually be decided chemically. In all cases, the metal-nitrogen bond distances indicate appreciable multiple bond character as would be expected for considerable back donation from the metal to the NO group.

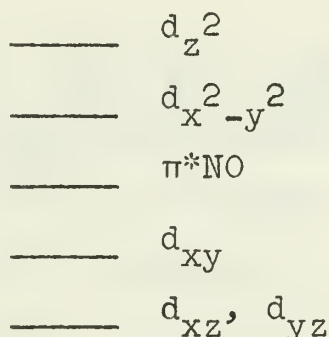
In addition, techniques such as electron spin resonance, optical spectra and Mössbauer data have been used in efforts to clarify the bonding. For the most part, they have been used to substantiate a particular molecular orbital scheme and the possible electronic structures. The bulk of this work has been done with the metal pentacyanonitrosyls. Here it is of interest to determine the relative strengths of π -bonding and the extent and location of electron delocalization.

MOLECULAR ORBITAL DESCRIPTION OF CYANONITROSYLS

The cyanonitrosyls are among the most numerous anionic nitrosyls. Since the cyanide ion has one of the largest capacities for inducing spin pairing, the majority of the compounds are diamagnetic or have low magnetic moments. Although the cyanonitrosyls are considered octahedrally coordinated, obeying the inert gas rule, in only one case, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ (10), has the crystal structure been determined.

Gray and coworkers (11) have described the bonding in several metal nitrosyl complexes in terms of a molecular orbital approach. They have considered the nitroprusside ion, the parent member of a series of pentacyanonitrosyl complexes, in detail (12). The octahedral ion possesses approximately C_{4v} symmetry with an axial compression resulting from a very short Fe-N bond distance of 1.63 Å. This short bond distance confirms that the NO group is strongly coordinated to the metal. As a result the Fe-NO bond is assumed to dominate in the overall structure of the nitroprusside. This assumption is in agreement with Mössbauer work (13, 14) but contradictory to the assignment of π -bonding ability from infrared data (15). However, additional supporting evidence comes from optical spectra (13) and another infrared study (16).

Using the concept of the dominant Fe-NO bond, a molecular orbital treatment gave the d-level ordering of $d_z^2 > d_{x^2-y^2} > d_{xy} > d_{xz}, d_{yz}$. A level derived mainly from π^* NO separates the e_g and t_{2g} levels. The proposed ordering is



After a d^6 configuration, the electrons are added to molecular orbitals derived mainly from π^* NO. Then in d^7 and d^8 systems, there may be a gradual transition to bonding of NO and NO^- . Compounds with one or two electrons in the π^* NO level are predicted to have a bent M-N-O grouping. Gray and Manoharan (17) have made an extensive study of the optical spectra of several metal pentacyanonitrosyls and have assigned the electronic absorption bands on the basis of this energy level diagram. Electron spin resonance data also show agreement with the proposed scheme (18).

Symons and coworkers (19) have disagreed with the relative ordering of the energy levels in Gray's scheme. They claim that the formal positive charge carried by the nitrosyl ligand requires a modification. As a result, they propose $d_{x^2-y^2} > d_z^2 > d_{xy} > d_{xz}, d_{yz}$. Their assignment

is supported by electron spin resonance studies indicating that the unpaired electron in $\text{Fe}(\text{CN})_5\text{NO}^{2-}$ is localized in an orbital (mainly d_z^2) on the iron (20).

These authors also propose a non-linear M-NO group in which the major factor governing the M-N-O angle is the population in the d_z^2 orbital (19). Major deviation from linearity would occur when the d_z^2 level is filled and have a precedent in $\text{Co}(\text{NO})[\text{S}_2\text{CN}(\text{CH}_3)_2]_2$ where the Co-N-O angle is about 135° (21). The Cr-N-O angles in $\text{C}_5\text{H}_5\text{ClCr}(\text{NO})_2$ are 166.4° and 170.8° (22) which the authors ascribe to electrostatic interactions in addition to an electronic factor. Other bent M-N-O groups occur in the nitrosyls but none are as large as 135° and the authors tend to attribute the deviations to crystal packing effects rather than to any electronic factor.

CONCLUSION

The field of bonding in nitrosyls still contains many uncertainties. Particularly with the cyanonitrosyls, the situation is improving with the molecular orbital concepts. It is likely that similar unification will be obtained when other groups of nitrosyls become the subject of molecular orbital studies. Much of the difficulty in nitrosyl bonding lies in the lack of structural data on bond angles and bond distances. This prevents the establishment of a firm basis on which to carry out theoretical work.

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It is necessary to consider the various factors which influence the results of the investigation in order to obtain a correct interpretation of the data.

The results of the investigation are presented in the following tables. The first table shows the results of the investigation of the effect of the concentration of the solution on the rate of reaction. The second table shows the results of the investigation of the effect of the temperature on the rate of reaction. The third table shows the results of the investigation of the effect of the catalyst on the rate of reaction.

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TABLE I

Effect of concentration of solution on rate of reaction

Concentration of solution (M)	Rate of reaction (mol/l.s)
0.1	0.001
0.2	0.002
0.3	0.003
0.4	0.004
0.5	0.005

TABLE II

Effect of temperature on rate of reaction

Temperature (°C)	Rate of reaction (mol/l.s)
20	0.001
30	0.002
40	0.004
50	0.008

TABLE III

Effect of catalyst on rate of reaction

Catalyst (M)	Rate of reaction (mol/l.s)
0	0.001
0.01	0.002
0.02	0.004
0.03	0.006

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ENERGY LEVEL ORDERING AND ELECTRON DISTRIBUTION IN π -METALLOCENE COMPLEXES

R. W. Lauver

November 8, 1966

INTRODUCTION

The nature of the bonding in π -metallocene complexes such as ferrocene, $(C_5H_5)_2Fe$, and dibenzene chromium, $(C_6H_6)_2Cr$, has been a topic of considerable interest for several years. In particular, the ordering of the electronic energy levels and the distribution of charge within these molecules have been points of some controversy. Since both of these problems have been approached by several investigators along several theoretical and experimental paths, it seems appropriate here to review and compare the results attained to this time.

The high symmetry of these molecules has allowed the application of several simple models of LCAO-MO theory in describing the bonding (1). The energy levels of interest--those highest energy filled orbitals and lowest energy unfilled orbitals which are instrumental in determining magnetic and spectroscopic properties--have much of the character of metal d-orbitals and have been treated as such in several ligand field calculations of their relative energies. (Note: in D_{5d} and D_{5h} point groups, the metal orbitals have the symmetries a_{1g} : s, d_{z^2} ; e_{1g} : d_{xz} , d_{yz} ; e_{2g} : d_{xy} , $d_{x^2-y^2}$; a_{2u} : p_z ; e_{1u} : p_x , p_y .)

ORDERING OF ENERGY LEVELS

The MO calculations that have been carried through (1-8) have been reasonably successful in predicting many structural and chemical properties of these molecules, but have not led to a resolution of the point in question.

The quantitative approximations of ferrocene orbitals by Dahl and Ballhausen (8) (D-B), Shustorovich and Dyatkina (4) (S-D), and R. D. Fischer (8) are indicative of the variations in results that have been obtained. Their results (ordered in increasing energy):

D-B : $[\dots a_{1g}' < e_{1g} < e_{2g}] < e_{2u} < 2a_{2g}^* < e_{1g}^* \dots$

S-D : $[\dots e_{1g} < a_{1g}' < e_{2g}] < a_{1g}^* < a_{2u}^* < e_{1u}^* < e_{2u} < e_{2g} < e_{1g}^*$

Fischer: $[\dots e_{1u} < e_{2g} \approx a_{1g}'] < a_{2u}^* \approx e_{1g}^* < e_{2u} \dots$

(Filled orbitals are bracketed.)

The disagreement in ordering is most evident in those orbitals of d-character (a_{1g}' , e_{2g} , e_{1g}^*). The changes in predicted ordering are due primarily to the sensitivity of the MO energies to

- 1) choice of energies for the metal and ring atomic orbitals.
- 2) extent of mixing of higher energy metal orbitals (in particular the 4s and 4p orbitals).
- 3) method of approximating off-diagonal matrix elements (primarily the estimation of overlaps).

Among the crystal field descriptions of metal orbital splitting (9-11), a recent calculation by Scott and Becker (11) is of most interest. They use experimental transition energies to determine the crystal field parameters and then calculate the d-orbital ordering to be $e_{2g} < a_{1g}' < e_{1g}^*$ for ferrocene.

It would seem that the most probable description of these orbitals is $e_{2g} \approx a_{1g}' < e_{1g}^*$, for most metallocenes. The near degeneracy of the two lower levels (the highest filled levels in most compounds) can result in changes in their ordering as ring and metal orbital energies change (for example, the configuration of ferrocene would be $(a_{1g}')^2(e_{2g})^4$ while that of dibenzene chromium would be $(e_{2g})^4(a_{1g}')^2$), and can lead to high spin felling of the orbitals (as in chromocene, $(C_5H_5)_2Cr$, with configuration $(e_{2g})^3(a_{1g}')$ (7)).

The most straight forward methods of checking these results is to compare the predictions with observed spectral and magnetic data. This has been done for several compounds (7,12,13) (in particular detail for ferrocene) and general agreement can be attained. The uncertainties associated with these approximations still do not allow one to make distinction between various ordering schemes on this basis.

ELECTRON DISTRIBUTION

The distribution of electrons between the metal and the rings is closely allied with the ordering of the energy levels, and the uncertainties in one are reflected in the other. A major point of contention is whether the net effect of bond formation is delocalization of ring π -electrons to the metal or metal d-electrons to the rings.

Qualitative estimates of charge delocalization can easily be made (1), but the large number of factors involved (many are competitive) allow no conclusion to be drawn. Electron population calculations have been performed for several of the MO models (6,14), but again disagreements arise. (For example, in ferrocene, the net charge of Fe is predicted to be +0.686 by S-D (4), but -0.690 by D-B (14)). S-D have shown in their calculations on a series of such compounds a consistent change of charge density that can be correlated with the metal concerned and its oxidation state (6). They invoke chemical and spectral observations to support their argument, but the arguments of the opposition seem equally well based (2).

Experimental estimates of electron densities obtained from ESR and NMR data indicate that electrons are delocalized onto the rings (15-18). Some attempts to calculate field gradients for Fe in ferrocene from predicted charge densities have been employed to check the validity of the predictions (14,19).

The precisions of both theoretical and experimental data still do not allow one to satisfactorily determine ordering of the energy levels nor the true distribution of charge. Probably, the most desirable advance that could be made now would be a more precise calculation of molecular orbitals.

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MAGNETIC PROPERTIES OF METAL AMMONIA SOLUTIONS

Vince Magnuson

November 10, 1966

INTRODUCTION

Approximately 100 years ago Weyl discovered that alkali metals dissolve in liquid ammonia. Since that time the following physical properties of these metal solutions have been extensively studied: (a) optical; (b) photoelectric; (c) electrical; (d) thermoelectric; (e) magnetic. Although over a thousand papers have been presented on this general topic, the general nature of the structure of these solutions remained a mystery until the early 50's. Then, by the use of paramagnetic resonance, nuclear magnetic resonance, and static susceptibility studies, some acceptable models have been proposed. The purpose of this seminar is to discuss some of the magnetic studies of metal-ammonia solutions and to investigate the models that these studies suggest.

PROPOSED MODELS

Many models have been proposed to explain the nature of the structure of the metal-ammonia solutions (1). These models can be grouped into the following three main divisions: (a) primitive cavity (2) (polaron); (b) cluster (3) (monomer); (c) unified (a combination of the first two). The primitive cavity model proposes that both the unpaired electrons and the metal cations are trapped in approximately spherical cavities (different cavities) formed by ammonia molecules, whereas the cluster model proposes that the cation and the unpaired electron are trapped in the same cavity forming the basic unit called a monomer, M.

MAGNETIC PROPERTIES

Total Susceptibility. If the unpaired solvated electrons do not interact with each other, then the "molar" magnetic susceptibility of the metal solutions should be independent of concentration. However, Huster (4) in 1947 and Freed and Sugarman (5) in 1948, reported that the total molar susceptibility decreases with increase in concentration. This decrease in χ_m with increasing concentration was interpreted as occurring due to pairing of spins of the solvated electrons. Also, these investigators noted that the susceptibilities increased with increasing temperature at all concentrations studied and that in very dilute solutions the molar susceptibility approached that of the value of the susceptibility of an Avogadro's number of free spins ($N\mu_0^2/kT$). Thus, their data imply that whichever model is correct, it must allow for electron pairing, which could be accomplished in the cavity model by forming e_2 centers and in the cluster model by forming dimers. Thus either model can explain the pairing.

Electron Spin Resonance. With the invention of the magnetic resonance technique, a powerful tool for experimental investigation of these solutions became available. Because the resonance method can provide detailed information about the microscopic environment of these unpaired electrons and nuclei, such data should be and are an important basis for theoretical models. The electron spin resonance in metal ammonia solutions has been observed and measured by a number

of workers, using various solute metals and working in various concentration ranges and temperatures. (6-10).

The total susceptibility measured for a given material will consist of contributions from both paramagnetic and diamagnetic susceptibilities, where the former is the larger of the two. Static field measurements give only the sum of the two contributions whereas the paramagnetic resonance experiment can be used to give χ_s , the value of spin paramagnetic susceptibility. Thus, Hutchison and Pastor (1,6) used their ESR results to obtain some information on the diamagnetism of the electron in the cavities. They found that χ_s was just slightly larger than χ and obtained a value for the orbital diamagnetism ($\chi_s - \chi$) at 0.5M and -33° C of $26 \cdot 10^{-6} \text{ mole}^{-1} \text{ cm}^3$. Using this value, they calculated a mean value of r^2 , $\{\langle r^2 \rangle\}^{1/2}$, for the orbital in which the electron moves of 3.0A.

The quantity g , defined by the basic ESR equation, $h\nu = g\beta H$, has been found to be nearly constant for all metal solutions and has a value less than that for the free electron (6, 7, 8). In a study of K-NH₃ systems by Hutchison and Pastor, the spectroscopic splitting factor was (a) independent of concentration, (b) the same at different frequencies, $70 \cdot 10^8 \text{ cycles sec}^{-1}$ and $23.5 \cdot 10^4 \text{ cycles sec}^{-1}$, and (c) has a value of $2.0012 \pm .0002$. They concluded that the unpaired electron is bound in the same manner in all concentrations. Kaplan and Kittel (2) indicated that this is compatible with bonding on the protons of the NH₃ molecules surrounding the cavity, in analogy with the bonding that has been found to exist by magnetic resonance for electrons trapped in vacancies in alkali halide crystals (F centers). Das (1) explained the observed independence of the g factor on the metal ion in two ways: (a) either the observed g value is due to cavities and resonance from monomers is too broad to detect; or (b) the signal is a weighted average of the two models.

The outstanding feature of the ESR spectra is its extraordinary sharpness in dilute metal solutions (possibly the sharpest line ever observed in ESR work). The absorption line is very close to Lorentzian in shape and has a width (δH) as narrow as 0.02 gauss (6,8). Observed first by Hutchison and Pastor, the explanation of ESR spectra was then proposed by Kaplan and Kittel using the cavity model. They deduced that only the protons contribute to the hyperfine interaction leading to a width of about 10 gauss which was then motionally narrowed to ~ 0.02 gauss by the rotation and diffusion of ammonia molecules. Kaplan and Kittel (2) and Levy (8) presented the cavity model as one in which the unpaired electron existed entirely in delocalized molecular orbitals on all of the protons which define the cavities.

Nuclear Magnetic Resonance. Application of nuclear magnetic resonance should reveal some information about the nature of the centers in which the unpaired electron exists. However, the first such NMR studies, carried out by McConnell and Holm (11) in 1957, were rather limited in their value for prediction of a model for dilute solutions since no NMR signal was obtained when the concentration was less than 0.04 M. Since that time O'Reilly (12) has succeeded in studying metal NMR and ^{14}N NMR in very dilute concentrations.

Knight shifts were measured by O'Reilly for ^7Li , ^{23}Na , ^{87}Rb , ^{133}Cs , and ^{14}N in ammonia solutions for a variety of temperatures and concentrations. The Knight shift, k , is defined as $(H_r - H_s)/H_r$ where H_r is the magnetic field for which resonance occurs in the reference solution and H_s , the field for which resonance occurs in the metal ammonia solution at fixed frequency. The resonance frequencies for ^{14}N and ^{23}Na nuclei as well as the other nuclei were appreciably shifted from frequencies in pure ammonia and aqueous sodium bromide solution, respectively, and were larger by a factor of 10 than the chemical shifts observed for these nuclei in chemical compounds. These fractional shifts $\Delta H/H, (\Delta\nu/\nu)$ of a nuclei species in a metal ammonia solution are considered to arise from the isotropic hyperfine interactions between unpaired electrons and the nuclei of interest. The Knight shift can then be used to calculate the total average electron spin density at a nucleus N , $\langle |\psi(N)|^2 \rangle$ by means of $k(N) = \frac{8}{3}\pi \left(\frac{\chi_v^{\text{sp}}}{N} \right) \langle |\psi(N)|^2 \rangle_{\text{av}}$. In addition, Knight shift data can be used to obtain nuclear spin densities at the unpaired electron, giving information as to the nuclei responsible for relaxation in ESR experiments. O'Reilly found the ^{14}N spin density at the unpaired electron is essentially independent of the alkali metal and concentration up to 0.6M and equal to $0.88 \pm 0.11 a_0^{-3}$ at 300°C and also that the electron spin density at ^{23}Na was $8 \cdot 10^{-3} a_0^{-3}$ and approximately independent of temperature and concentration. The proton shift was too small to measure within the resolution of the NMR spectrometer, and Holm indicated that in the upper limit it even has the opposite sign from the shift for ^{23}Na and ^{14}N . The observation of the above finite alkali metal shift is one of the strongest points in favor of the existence of the cluster monomer. However, the ^{14}N shift can be explained by both the cavity and cluster models. O'Reilly interpreted the observed concentration and temperature dependence of $k(\text{Na})$ by assuming the existence of both cavities and monomers of the type M and M^- .

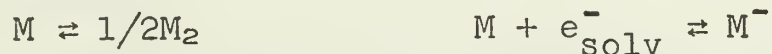
Kaplan and Kittel considered the protons to be the leading contributors to the ESR line width, but from the NMR data we can see that this is not true because of the negligible Knight shift found for the protons. Thus, with this in mind, Pollak (9) proposed that his ESR data was consistent with a cavity model in which the primary relaxation was due to the contact hyperfine interaction of the electron with the ^{14}N nucleus, modulated by the relative motion of the electron and ammonia molecules. Pollak found that T_1 equals T_2 for all concentrations and temperatures and that these relaxation times ranged from 1 to 3 μsec by using the fact that for a Lorentzian absorption line $T_2 = 2[\gamma^2 \gamma(\delta H)]^{-1}$ where γ , the gyromagnetic ratio of the electron, has the value of $17.6 \cdot 10^6 \text{ oe}^{-1} \text{ sec}^{-1}$. Using the Bloembergen, Purcell, and Pound (13) theory of motional narrowing, Pollak calculated a value for T_2 of $2.9 \cdot 10^{-6} \text{ sec}$ which agrees well with experiment. Pollak also looked at the spin relaxation time of deuterated metal ammonia solutions and again concluded that the relaxation proceeds via contact with ^{14}N and not via protons or deuterons. In a recent paper, Culter and Powles (10) agreed that the primary spin relaxation mechanism was due to a modulated scalar interaction with ^{14}N nuclei. They obtained, however, a questionable estimate based on relaxation times of the effective number of ^{14}N nuclei which they say excludes the cavity model.

ESR of Europium-Ammonia Solutions. Upon dissolution of europium in ammonia a blue solution results that resembles that of alkali-metal solutions. These solutions provide a unique opportunity to simultaneously observe the ESR spectra of both the solvated electron species and europium ions, since the europium ion Eu^{+2} is also paramagnetic. The electron spin resonance spectrum (7, 14) consists of a single line characteristic of the solvated electron and a complex hyperfine pattern which is shown to arise from Eu^{+2} , $^8\text{S}_{7/2}$. The g value observed for the single line was 2.0014 ± 0.0002 agreeing with those observed for the alkali metals. Catterall and Symons (7) concluded that the detection of separate ESR spectra for Eu^{+2} ions and solvated electrons in these solutions shows that in ammonia, cation-electron interaction involves loose ion pairing rather than monomer formation.

ESR of Metal-Amine Solutions. ESR spectra of metal-amine solutions that show a nuclear hyperfine splitting were first reported by Dye (15). The g values were reported to be 2.0018 ± 0.0002 . Bar-Eli and Tuttle (16) reported that although K does not show any evidence of the solvated cavity electron in K-ethylamine solutions, it does show a four line spectra attributed to K-electron contact interaction. On the contrary, they found that Li, Cs or Rb-ethylamine solutions gave a nine line pattern and one sharp singlet line attributed to the solvated electron. This behavior was interpreted by their introduction of a modified view of the Becker, Lindquist and Alder model which included additional equilibrium equations involving spin exchange, electron exchange and exchange of solvent molecules.

CONCLUSION

The best overall model describing the properties of alkali-metal solutions in ammonia is given in terms of the following equilibria



where M^+ is the metal cation, M is either an ion-pair ($\text{M}^+_{\text{solv}} \cdots \text{e}^-_{\text{solv}}$) or monomer, M_2 is a dimer or a cluster of four ions, and M^- is the two electron spin-paired analogue of the ion-pair or of the monomer. Most data can be explained using any or all of the above.

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BONDING IN TRANSITION METAL FLUORIDE COMPLEXES

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INTRODUCTION

Crystal field theory has had a long and varied history ever since Bethe published his classical paper showing that a degenerate electronic configuration of an ion must break up into two or more states under the electrostatic perturbation of a crystal lattice. The defining feature of this theory is its assumption that all interactions between an ion and its surroundings may be treated as purely electrostatic interactions between point charges. When treated as a semi-empirical theory, with the crystal field splitting $10Dq$ considered as an adjustable parameter, it has been highly successful in fitting experimental data; when considered as a fundamental theory for the behavior of transition metal ions in crystalline fields, it has been strikingly unsuccessful in predicting from first principles, the fundamental parameter $10Dq$ (1). Ligand field theory has attempted a more sophisticated treatment using crystal field theory as a good zero-order approximation. Van Vleck discussed a transition metal ion consisting of a central ion with an unfilled $3d$ shell surrounded by six ligands arranged in a regular octahedron. He showed how the mixing between the $3d$ orbitals and the $2p$ orbitals of the ligands could produce a contribution to the crystal field splitting which was to be added to the splitting produced by the static cubic potential (2). His calculations gave the proper sign of $10Dq$, and by using Slater orbitals for the $3d$ -electron functions, the values of $10Dq$ were quite close to experimental measurements (3). Following the pioneering computations of Van Vleck and others, a series of theoretical investigations succeeded in pinpointing the basic shortcomings of existing theory, and indicated the need for a multi-electron, many-centered, molecular orbital approach (4).

The purpose of this seminar is to review some of the experimental work on fluoride complexes of the type KMF_3 and K_3MF_6 using NMR and ESR methods. The nature of the transferred hyperfine interaction will be discussed from a molecular orbital point of view. Since the most significant theoretical work has been in the area of ab initio calculations (4,5), the bonding in these complexes will be discussed with reference to this. The mathematical methodology of the MO approach will be described qualitatively; semiempirical MO methods will not be discussed except in passing.

THEORY

The results of both ESR and NMR experiments on octahedral transition metal fluoride complexes indicate that spin from the $3d$ orbitals of the metal is surprisingly delocalized onto the fluorine ligands. Since fluorine has a nuclear spin ($I=1/2$), this transferred hyperfine interaction is observable by magnetic resonance methods. Although these complexes are essentially ionic, the delocalization is most easily described in terms of molecular orbital theory; the bonding may be interpreted in terms of the coefficients of the fluorine atomic orbitals. In the traditional LCAO description the valence shell orbitals of the ligands are used as a basis for a

representation of the point group (O_h) of the molecule, and this representation is decomposed into its component irreducible representations. The fluorine 2s and 2p orbitals are then combined into linear combinations belonging to these irreducible representations, and the interactions between ligand and metal orbitals of the same symmetry are computed. The energies obtained are then used to make linear combinations of the metal and ligand orbitals which are the true MO's of the complex. The results can be summarized in the familiar MO diagram.

In MO terminology, to the extent to which bonding occurs, the unpaired electron in the antibonding orbital has the character of the fluorine functions and consequently a strong hyperfine interaction with the nucleus is observed. This is expressed by the Hamiltonian $H=I \cdot A \cdot S$ in which I is the fluorine nuclear spin, S the metal ion electron spin, and A the hyperfine interaction tensor. Theoretical interpretations of the hfs (hyperfine structure) observations have followed several distinct models which describe the unpairing as being the result of (1) an admixture of covalent bonding into the purely ionic configuration or (2) the unpairing action of the Pauli principle (on the ionic configuration) which affects those fluoride orbitals having the same spin as the cation 3d orbital differently from those orbitals having opposite spin. In either method the unpaired F^- s-electrons produce an isotropic hfs (from the contact part of the Fermi interaction) whereas the 2p-electrons are responsible for the anisotropic interaction (6). The isotropic and anisotropic coupling constants provide the basis for determining the fractions of σ -, π -, and π -bonding in the complexes studied.

EXPERIMENTAL

The O_h symmetry of fluoride complexes greatly lessens the experimental and computational difficulties in interpretation of transferred hyperfine interactions because the $p\pi$ orbitals from the fluoride ion have the same contribution. Shulman and Knox (7) in studying $KNiF_3$ and K_2NaCrF_6 found the resonance anisotropy out of line with previous results found for $KMnF_3$. They concluded that measurement of the F^{19} hyperfine interaction only determines the difference in occupancy of the $p\sigma$ and $p\pi$ orbitals, i.e. $f_{\sigma}-f_{\pi}$; in Mn^{+2} with a d^5 configuration, all five of the one-electron functions are half-filled, and these unpaired spins are available to form both σ - and π -bonds with the ligands. However, in Ni^{+2} (d^8) the configuration is split by an octahedral ligand field so that the t_{2g} triplet lies lower and is completely filled while the e_g doublet is a half-filled subshell. Since the triplet mixes with the ligand functions to form π -bonds and the electrons in the doublet mix to form σ -bonds, it is clear that the magnetic electrons in Ni^{+2} only mix to form σ -bonds. Similarly Cr^{+3} (d^3) can only form π -bonds. Helmholz (8), however, found that isotropic interaction parameters were not zero as required by simple MO theory for d^3 systems. He postulated the contributions of higher states through configuration interaction to explain this discrepancy.

Hall et. al., investigating the ESR spectra of iron group impurity ions in O_h sites in cubic fluoride crystals, found that σ - and

π -bonding are of comparable magnitude in d^3 , d^5 , and d^8 systems, an observation confirmed by a variety of workers (10,11). They later concluded the same thing to be true for d^6 and d^7 systems (12). Thornley et. al. have studied the ESR of $\text{Co}^{+2}:\text{KMgF}_3$ and have determined independently the three bonding parameters: $f_s = .54 \pm .03\%$, $f_\sigma = 2.9 \pm 1.0\%$, $f_\pi = 1.9 \pm 1.0\%$. The uncertainty of bonding fractions in this case is dispelled since the Co^{+2} ground state allows all three admixtures to occur without cancellation (in comparison with d^3 , d^5 , and d^8 systems). These authors restrict themselves to valence electrons, neglect electron transfer, and recognize that uncertainty in the size of the spin-orbit coupling coefficient for Co^{+2} in the crystal probably leads to large errors in f_σ and f_π . Gladney (13) recently obtained results for Co^{+2} which are within Thornley's confidence limits but are at variance with the suggestion that for octahedral Co^{+2} σ - and π -bonding are of comparable magnitude: $f_s = .61 \pm .02\%$, $f_\sigma = 3.9 \pm 0.3\%$, and $f_\pi = 0.9 \pm 0.3\%$. In other words, σ -bonding is significantly larger than π -bonding in this case. By way of contrast, Kuska and Rogers (14) in an ESR study of C^{13} enriched $\text{Cr}(\text{CN})_6^{-3}$ concluded that this ion has appreciably more covalent σ -bonding character than CrF_6^{-3} but that π -bond covalent character is about the same.

DISCUSSION OF RESULTS

It was not long before the discrepancy between results of transferred hyperfine experiments and predictions on the basis of theoretical models became painfully apparent. Several theoretical papers are particularly noteworthy and relevant to this discussion.

Freeman and Watson (6) suggest that previous interpretations have neglected important terms in describing the spin density at the fluorine nucleus. The unpairing action of the $1s$ -electrons is usually disregarded on the grounds that the $1s$ - $3d$ overlap is much smaller than the $2s$ - $3d$ overlap. But $|\varphi_{1s}(0)|^2$, the Fermi contact term for the $1s$ electron, is appreciably larger than $|\varphi_{2s}(0)|^2$. These authors suggest that terms such as $\psi_{3d}(r_F)$, the magnitude of the metal ion $3d$ function evaluated at the fluorine nucleus, have been neglected and may be significant.

Marshall and Stuart (2) expanded on this work and discuss ligand field theory in terms of an essentially ionic Heitler-London model which they feel is justified for the ionic fluoride complexes. This theoretical model requires wavefunctions be found by the variational method, and seems to be more realistic than Hartree-Fock free-ion wavefunctions which assume no interaction between ions. It is suggested that the nephelauxetic effect which is a screening effect arises from a strong distortion in the outermost part of the wavefunction. However, a simple radial expansion of the wavefunction is only a first approximation to the true distortion, which is quite serious for the tail of the d wavefunction, i. e. in region of the fluorine nucleus. The cardinal difficulty in interpreting hfs is, therefore, the fact that the overlap integral ($d/1s$) cannot be calculated with any accuracy. Calculations of coupling constants based on the model are best if the $1s$ orbital is ignored. The authors conclude that no theory of hfs will be satisfactory until contribution from the $1s$ -electron is properly computed. Additional corrections

of theory are suggested for ions with other than half-filled d-shells, i.e. have non-spherical symmetry. Spin-orbit coupling becomes a problem as well as unquenched orbital momentum which requires a correction to the dipole-dipole interaction.

In a classical series of papers (5,15), Shulman and Sugano criticize Marshall and Stuart for assuming $f\pi=0$ in their essentially ionic model and suggest that overlap alone does not account for observed hfs. In addition they found the concept of expanded d-electron radial functions to be unnecessary in explaining some observations and inadequate in explaining others. In a study of covalency in KNiF_3 , they calculated $10Dq$ (the energy difference between the e_g and t_{2g} antibonding levels) from first principles using Hund-Mulliken-Van Vleck MO theory. Their ab initio attempt in calculating $10Dq$ was very successful (6350 cm^{-1} calc.; 7250 cm^{-1} exp.) although many of their approximations have been severely criticized. The calculation further showed that while π -bonding in KNiF_3 is almost as large as the σ -bonding, it is only important whenever the wavefunctions themselves are important (e.g. in hyperfine interactions), but it is not as important as the σ -bonding when bond energy is involved. Both authors in recognizing their approximations, felt "their main result lies in the physical understanding of the crystal, not in any particular agreement between a calculated number and a measurement."

Watson and Freeman (4) criticize the whole theoretical basis for the preceding work, suggesting that only covalent mixing of bonding electrons having no antibonding partners can contribute to experimental observables. According to them the covalency (not overlap) of antibonding electrons is entirely irrelevant because it is exactly compensated by the covalency of their bonding partners. In recalculating $10Dq$ from first principles using the cluster model, they showed the incomplete Hamiltonian of Shulman and Sugano to be internally inconsistent, since orthogonality of bonding and antibonding wavefunctions could not be obtained; consequently, any quantitative estimate of covalent bonding parameters was rendered suspect. Furthermore, their "more correct" calculation gave an even lower $10Dq$ value of 2800 cm^{-1} . They suggested that perhaps the calculation can be improved by including bulk expansion or contraction of metal (ligand) orbitals, correlation effects, or even by disregarding the cluster model itself. Several recent investigations have sought to include electron correlation by allowing for configuration interaction within the context of either a Hartree-Fock (16,17), or Heitler-London (18) theoretical framework. The greatest difficulty at the moment seems to be that a priori calculations of covalency present such formidable computational problems that an accurate estimate of the theoretical implications of the model (particularly that constructed from Hartree-Fock free-ion orbitals) is not even available.

CONCLUSION

In view of these problems, Gladney (13) made the observation that the object of ab initio theories of electronic structure should be to reproduce measures of covalent bonding which are independent of the AO basis chosen, rather than to describe bonding in terms of fractional occupations. These have a built-in theoretical bias as well as no good physical basis, and even within the model employed are extremely uncertain.

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OPTICAL SPECTRA OF SOME TRANSITION METAL IONS
IN THE CORUNDUM LATTICE

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INTRODUCTION

The purpose of this seminar is to present an analysis of the interpretation of solid state electronic absorption spectra of some transition metal ions substituted into the Al_2O_3 lattice. Some of the general aspects of the information which can be obtained from the absorption spectra-calculation of the crystal field parameter Dq , the Racah parameters B and C , fine structure analysis, assignment of the observed bands to specific transitions, etc., will be discussed.

PRELIMINARY PHYSICAL DATA

The crystal structure of Al_2O_3 (Corundum) was first performed by Pauling and Hendricks (1) in 1925, and a later refinement of the structure by Newnham and deHaan (2) appeared in 1962. The oxygen ion positions approximate a hexagonal close pack system with the trivalent aluminum ions occupying two-thirds of the octahedral interstices (3). The true site symmetry of the aluminum ions is C_3 , but for much of the spectroscopic analysis, the assumption of C_{3v} symmetry for the cation site has been used.

$\text{Ti}(\text{III}): \text{Al}_2\text{O}_3$ SPLITTING OF THE OCTAHEDRAL STATES UNDER A TRIGONAL FIELD PERTURBATION

As was noted in the previous section, the symmetry of the cation site into which the foreign ion is introduced is less than octahedral. In accordance with standard group theoretical techniques, the symmetry states of the $\text{Ti}(\text{III})$ ion in a field of trigonal symmetry are obtained by first considering the effect of a hypothetical octahedral field on the free ion states, and then considering the trigonal field as a perturbation on these levels. Three final states for the $\text{Ti}(\text{III})$ ion result, two having symmetry E and one having symmetry A_1 in the point group C_{3v} .

The relative ordering of the levels in the trigonal field can be determined from the polarized crystal spectra. The selection rules (C_{3v} symmetry) for the two possible cases (A_1 or E ground state) are shown below. (Γ stands for a component of the electronic transition moment vector.)

(1.) $A_1 \rightarrow E$

$A_1 \times \Gamma \times E = \Gamma \times E$. Since the direct product $A_1 \times \Gamma \times E$ must contain A_1 in order to be of a finite value, Γ must belong to the irreducible representation E . The transition will be (x,y) or perpendicularly polarized with respect to the three-fold axis of the crystal (z).

(2.) $E \rightarrow E$

$E \times \Gamma \times E = (E + A_1 + A_2) \times \Gamma$. Γ may belong to either the $A_1(z)$ or $E(x,y)$ irreducible representations. The band will appear in both the parallel and perpendicular spectra.

The observed spectra shows a much stronger parallel than perpendicular polarization, indicating that the ground state has E symmetry. Spectra up to 1000°K show little change in the polarization ratio, indicating a minimal population of the A_1 state up to 1000°K and a trigonal field parameter, v , of $>1000 \text{ cm}^{-1}$. The effect of pressure along the three-fold axis on the spectra and the crystal field parameters has been discussed by Minomura and Drickamer (6).

V(111): Al_2O_3 EVALUATION OF THE TRIGONAL FIELD PARAMETER V AND VIBRATIONAL FINE STRUCTURE IN AN ABSORPTION BAND

The solid state spectra of V(111) in corundum has been examined by several authors (4-13). Within the strong field approximation three electronic states are to be considered for the d^2 case, t^2 , te , and e^2 , listed in order of their expected energy. Pertinent energy level diagrams for the configurations t^2 and te under the influence of a field of C_{3v} symmetry appear in references (5) and (7). The trigonal field parameter, v , can be evaluated by measuring the splitting of the 3T_1 parent octahedral band. This separation has been measured by the use of polarized crystal spectra (4) and has been given a value of $380 \text{ cm}^{-1}(v/2)$. The value of v is then 760 cm^{-1} .

A theoretical evaluation in the mode of the ionic model (12) gives a value of -539 cm^{-1} for K (equal to $-v/3$). This compares to a value of -253 cm^{-1} from the experimental data above.

Rigorous interpretation of the band splitting (4) indicates that the separation of the 3T_1 band is a function of many parameters (spin-orbit coupling and Jahn-Teller distortions included) and may not be an accurate measure of the trigonal field (25,26).

The band appearing at approximately 16000 cm^{-1} (3T_2 , te) has some unusual properties:

- (1.) there is no apparent splitting of the band.
- (2.) there is no significant difference in the intensity of the parallel and perpendicular spectra.
- (3.) the band shows vibrational fine structure.

The $E(T)$ band is predicted to be much stronger than the $A(T)$ band from intensity calculations (4). A perturbation on the system that could account for the experimental data is a transfer of intensity from the $E(T)$ transition to the $A(T)$ transition.

This transfer of intensity through vibrational interaction is amenable to group theoretical analysis by consideration of the Herzberg-Teller Theory of vibronic transitions in polyatomic molecules (14, 15, 16). The major premise is that if a forbidden (or weakly allowed) transition can couple to an allowed transition through a vibrational mode, a transfer of intensity from the allowed band to the forbidden band can occur.

From first-order perturbation theory, the wavefunction for the A(T) state after mixing with the E(T) states can be written:

$$\Psi^1_{A(T)} = \Psi^0_{A(T)} + \sum_i \lambda_{AE} \Psi^i_{E(T)}$$

$$\lambda_{AE} = \frac{\langle \Psi_A | H' | \Psi_E \rangle}{\epsilon_E - \epsilon_A}$$

Where:

$$H' = \sum_a \left(\frac{\delta H}{\delta Q_a} \right) Q_a$$

ϵ_E = Energy of the E state

In order for λ_{AE} to be finite, $A \times \Gamma_{H'} \times E$ must contain Γ_1 the totally symmetric irreducible representation of the point group. Thus, $E \times \Gamma_{H'} = \Gamma_1$, which requires that $\Gamma_{H'}$ be of E symmetry. $\Gamma_{H'}$ may be replaced by Γ_Q (15), the representation of the perturbing normal mode. Therefore, the normal mode causing the mixing of the E(T) state and the A(T) state must be of E symmetry.

The infra-red and Raman spectra of corundum has been determined (18) there is a band of E symmetry at approximately 194 cm^{-1} .

This closely approximates the band separations of approximately $200\text{-}210 \text{ cm}^{-1}$ observed on the long wavelength side of the 3T_2 band.

Another perturbation on the 3T_2 excited state which can be invoked to explain the observed intensity ratio is a Jahn-Teller distortion of the equilibrium configuration (see reference(17) for a discussion of the Jahn-Teller Theorem from a group theoretical point of view). The assymetry of the charge distribution in the 3T_2 state makes it unstable to nuclear displacement (assumed to be the E normal mode because of its appearance in the spectra). The commonest type of Jahn-Teller Effect is a tetragonal distortion of the octahedron (distortion occurs along an axis at 54.7° to the trigonal C_3 axis). A calculation of the energy of the spectral band and its intensity under this type of distortion has been made (4) and fits the data.

A temperature study of the optical strength of the 3T_2 band was made (4) and allows a tentative assignment of the perturbing potential. At 77°K the parallel spectrum is approximately 75% as strong as the perpendicular spectra. However, at 700°K the intensity of the parallel spectra surpasses that of the perpendicular spectra. Using the vibronic intensity model, the best that can be expected is an equalization of the intensities of the parallel and perpendicular spectra. The temperature data, therefore, lends strong support to the Jahn-Teller distortion as the perturbing potential.

Cr(III): Al_2O_3 EVALUATION OF THE CRYSTAL FIELD PARAMETERS Dq , B and C

Wood, Ferguson, Knox and Dillon (19) have calculated the values Dq , B and C for Cr(III) ions in various octahedral fields. The disregard of the superimposed trigonal field of the corundum lattice in the calculation is in conflict with experimental and theoretical considerations. However, the techniques involved are illustrative and the results qualitatively correct.

The parameters to be calculated can be obtained from the assignment of three transitions in the experimental spectra. The three transitions and their assignments are given below:

Octahedral Designation	Energy Expression (20,21)	Experimental (cm^{-1})	Reference
${}^4A_2 \rightarrow {}^4T_2$	$10Dq$	18450	(4)
${}^4A_2 \rightarrow {}^4T_1$	$10Dq + 12B$	25200	(4)
${}^4A_2 \rightarrow {}^2E$	$9B + 3C$	14500	(22)

The initial values for Dq , B and C are found by solving the resulting linear equations.

$$10Dq = 18450$$

$$10Dq + 12B = 25200$$

$$9b + 3c = 14500$$

With suitable corrections for the effects of spin-orbit coupling and minor adjustments to the parameters by means of a computerized iteration process to obtain the best fit to the experimental data, the final calculated values for Dq , B and C are 1800, 640 and 3300 cm^{-1} respectively. The free-ion values are $Dq = 0.0$, $B = 920$ and $C = 3680 \text{ cm}^{-1}$. The fit to the experimental spectra is not of a high quality. This is to be expected considering the neglect of the trigonal field component in the calculations.

The decrease in the magnitude of B from the free-ion value has been correlated to the supposed expansion of the radial part of the d -orbitals on formation of the complex (23). This expansion of the radial distribution of the d -orbital wavefunctions has been attributed to covalency in the bonding between the metal ion and the ligands.

CONCLUSION

The analysis and assignment of the electronic solid state absorption spectra of transition metal ions in known lattices has shown itself to be a powerful technique for the understanding and

evaluation of the internal electronic structure of the transition metal ions studied. The ability to measure the polarized spectra in the solid state has provided much insight into the intensity mechanisms of d-d transitions.

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PROPERTIES OF COMPLEXES WITH TRANSITION METAL-GROUP III A- OR IV A-METAL BONDS

John L. Little

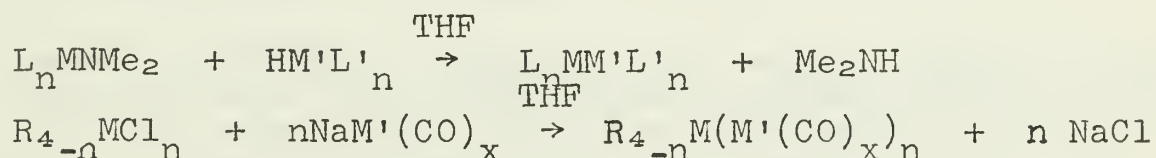
December 8, 1966

INTRODUCTION

Although Hein, et. al., (1) synthesized the first complexes containing groups IV A-transition metal bonds in 1941, there was almost no activity in this field until the early 1960's when interest was sparked by catalytic properties of platonic acid-stannous chloride solutions. Similarly for the analogous group III A complexes, the first paper appeared in 1942 (8) and no other research group published in this area until September, 1966 (9). Due to the newness of this field, most work has been synthetic, with few attempts to elucidate bonding or chemical and physical properties. The purpose of this seminar is to bring together the work to the present and attempt to point toward some possible future research.

SYNTHESIS

Metal-Metal bonds can be easily established between group IV A metals and transition metals which form reactive hydrides (2) or alkali metal salts (3), illustrated by the following general reactions: (M is gp. IV A metal and M' trans. metal throughout this abstract)



For transition metals of groups I and VIII, bonds to IV A are usually attained by reactions of IV A triorganolithium compounds with an organo-halide complex of the desired transition metal (4,5). Two novel exceptions are insertion of MCl_2 into bridged carbonyl complexes and expansion of a four coordinate iridium (I) complex to six coordinate iridium (III) by addition of $SnCl_3^-$ and H^- (6,7).

The only known group III A-transition metal complexes, those with cobalt carbonyl, have been synthesized by [1] reaction of a mixture of finely divided thallium or indium and cobalt with carbon dioxide at vigorous conditions (8) and [2] reaction of gallium and indium halides or thallium acetylacetonate with $Co_2(CO)_8$ or $NaCo(CO)_4$ (9).

CATALYSIS

Platonic acid-stannous chloride catalyst has been used for carbonylation of a variety of unsaturated compounds (11), hydrogenation of olefins (11), and isomerization of 1-pentene (12). In the case ethylene hydrogenation, from the fact that the ethylene proton NMR

resonance is shifted downfield on addition of catalyst, there is a fast exchange of free and coordinated ethylenes. Also the complex ion $[\text{HPt}(\text{SnCl}_3)_4]^-$ can be detected spectroscopically (10) in the catalyst solutions. Origin of the hydride ion is thought to be either the solvent alpha hydrogen or H_2 . Hydrogenation is thought to take place through a hydridoethylene-platinum intermediate, a common type of intermediate (21). Electrophilic attack by H^+ on the rearranged intermediate (ethylplatinum complex) yields ethane. Rate of reaction for a particular olefin depends on its ability to coordinate to platinum, which decreases for higher olefins. The rate of alkane formation is maximum for a tin to platinum ratio of greater than five to one. From such a solution $[\text{Pt}(\text{SnCl}_3)_5]^-$ was isolated as an insoluble salt of $[\text{Ph}_3\text{PMe}]^+$ (10). This unusual coordination number is undoubtedly stabilized by the electron withdrawing effect of SnCl_3^- , which gives rise to a large mesomeric trans effect, to be discussed in a later part of the seminar. As another example SnCl_3^- is known to stabilize a four coordinate gold complex, an unusually high coordination number for gold (15).

Properties of the platonic acid-stannous chloride as a hydrogenation catalyst suggest its use in the isomerization of olefins. It was found that isomerization of 1-pentene occurs only if hydrogen is introduced into the system (12). Thus hydride ion must originate from H_2 rather than the solvent (methanol) in this case. The preferred conformation of coordinated 2-pentene (C_1 and C_4 anti) gives rise to trans-2-pentene while a higher energy conformation (C_1 and C_4 syn) yields cis-2-pentene.

Very recently Schrauzer, et. al. (13), carried out the stereospecific dimerization of bicycloheptadiene using $\text{In}[\text{Co}(\text{CO})_4]_3$ as catalyst. In this case six CO groups are immediately eliminated by coordination of three bicycloheptadienes per catalyst molecule. The intermediate geometry is such that a new ring compound, "Binor-S", is produced. Thus two metallic centers (in this case cobalt) can lead to new and unusual transition state geometries for synthesis of stereospecific products as yet unknown.

STRUCTURE AND BONDING

There has been little structure work, and even less on bonding. Study of the polarity of Mn-Sn and Mn-Ge bonds in $\text{R}_3\text{MMn}(\text{CO})_5$ by reaction with various ethylene fluorides led to the proposal of a four-center rather than free radical reaction mechanism (17).

The sigma and pi bonding character of SnCl_3^- has been studied by F1⁹ shielding parameters of cis- and trans-trichlorostannato-m- and -p-fluorophenylbis(triphenyl-phosphine) platinum(II) (24). This study shows that the sigma-donor and pi-acceptor properties of SnCl_3^- are very much like those of carbon monoxide. Thus SnCl_3^- labilizes trans ligands and allows fast exchange at that site, a key requirement of catalytically active complexes.

From the fact that the proton-tin coupling constants are smaller for methyltin derivatives than for tetramethyltin (28), more s character is used by tin in the m-m bonds than in the three tin-carbon bonds. Thus the tin atom uses a higher degree of s character in its bonding to transition metals. This may be seen in $\text{Ph}_3\text{SnMn}(\text{CO})_4$ which has the following bond angles (25): Mn-Sn-C , $112.7 \pm 0.4^\circ$; C-Sn-C , $106.0 \pm 0.6^\circ$. These bond angles which should be the tetrahedral angle, widen with increased s character in the bond and decrease with decreased s character (as in the Sn-C bonds). The effect is even more pronounced in $\text{Ph}_2\text{Sn}(\text{Mn}(\text{CO})_5)_2$: C-Sn-C , 100° ; Mn-Sn-Mn , 117° (16).

Most of the infrared bands of $(\text{CH}_3)_3\text{SnMn}(\text{CO})_5$ have been assigned including CO stretch, M-C stretch and M'-C stretch (27), but the frequency of M-M' is too low to be seen in the range studied. The infrared active bands of the D_{2h} -SnR₂- or -PbR₂- bridged complexed $(\text{Fe}(\text{CO})_4\text{M}'\text{R}_2)_2$ were assigned as: M-C and C-O, $\text{B}_{1u} + 2\text{B}_{2u} + \text{B}_{3u}$; M-C-O, $2\text{A}_u + 2\text{B}_{1u} + 2\text{B}_{2u} + 2\text{B}_{3u}$; M'-C, $\text{B}_{1u} + \text{B}_{3u}$. As M' is varied from lead to germanium, there is a gradual increase in the carbonyl stretching frequencies. One would expect this since increasing electronegativity of M will increase the carbonyl bond order. Decreasing the electronegativity of R brings about a slight increase in carbonyl stretching frequencies (26).

REACTIONS

In the $\text{L}_3\text{MM}'\text{L}'$ systems, where M is a group IV metal and M' is a transition metal, possible points of attack by electrophillic, nucleophillic or neutral agents are the L-M, M-M' and M'-L' bonds. Also, M' can expand or contract its coordination number. Of course, degradation by heat and oxidation can occur.

Although no reactions have been carried out on group III transition metal complexes, they should show the same general types as above.

REACTIVITY

Lewis' and Nyholm's criteria (22) for tendency to form metal-metal bonds will be used in order to find general trends in reactivity as one varies M or M'. Those criteria for transition metals are:

- (1) greater tendency to form m-m bonds for higher oxidation states on the left of the transition series and for lower oxidation states on the right,
- (2) for a given oxidation state, stability increases to the left,
- (3) stability increases for second and third row transition elements,
- (4) ligands which reduce effective nuclear charge of the metal favor stabilized m-m bonds
- (5) maximum tendency to form m-m bonds occurs at molybdenum in the second row and around rhenium in the third row.

The criterion for formation of stable bonds between transition metals and elements with formal $d^{10}s^1$ configuration (as R_3Ge , R_3Sn and R_3Pb) increases as the electronegativity of the element; ie., from lead to germanium.

By some examples, it will be shown that in general IV-M' complexes follow the above trends. What little is known of III-M' complexes indicates that $Ta(Co(CO)_4)_3$ is less stable than $Ga(Co(CO)_4)_3$ (9). Hence one would expect to find the most stable m-m bonds between germanium or gallium and transition metals in the center and bottom of the transition series, notably molybdenum, tungsten and rhenium. No research has been published on these gallium compounds, and this seems as though it would be a very fruitful area. Also, results on catalytic properties of germanium-transition metal complexes has to my knowledge not been published. Attention has been restricted to the platinum metals, particularly platinum-tin complexes. Possible advantages of the Ge-M' complexes as catalysts are (1) reactions can be carried out under vigorous conditions without destroying the catalyst, and (2) R_3Ge^- is known to have a large inductive trans effect (23). Catalytic properties of III-M' complexes are almost totally unknown.

CONCLUSIONS

Investigations on the bonding in group IV-transition metal complexes are rare, with at least one group investigating changes in chemical properties on variation of L and M in $L_3MM'L'_n$ (17). Studies of physical properties, besides reporting the melting point, infrared spectrum and occasionally determined molecular weight, NMR spectrum or x-ray results are few in number. One could employ more sophisticated physical measurements such as ESR and Sn^{119} Mössbauer spectroscopy to elucidate m-m bonding in these complexes. Also m-m bond strengths could possibly be determined by the mass spectrograph.

The problem at hand for group III-transition metal complexes is obviously synthetic. The most stable complexes should be those with gallium-third transition series bonds.

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ELECTRON IMPACT STUDIES OF ORGANOMETALLIC COMPOUNDS: BOND DISSOCIATION ENERGIES

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Recently, research in the mass spectrometry of organometallic compounds has progressed at an extremely rapid rate. Pioneering studies involved the metal carbonyls, metal cyclopentadienyls, and silane and its alkyl derivatives. Mass spectrometry, as a physical method for elucidating structural problems and obtaining thermochemical data, has long been established as invaluable to organic chemistry. It is expected, therefore, to be useful in organometallic chemistry.

Assuming that the concept of the localized chemical bond is meaningful, substantial thermochemical information can be derived from experiment. The ensuing discussion will be primarily limited to bond dissociation energies and treated in two parts: A review of general principles, and a critical evaluation of results obtained thus far.

GENERAL PRINCIPLES

The main guide to interpreting electronic excitation processes is the concept of electronic states in which the potential energy of the nuclei varies with internuclear distance. For a diatomic molecule, AB, three types of vertical transitions (Franck-Condon Principle) can occur:

- (1) The formation of the AB^+ ion in various vibrationally excited states.
- (2) The transition to higher vibrational levels of the ionic state when a difference in internuclear distances is present.
- (3) The transition to a repulsive ionic state resulting in dissociation of the molecular ion:



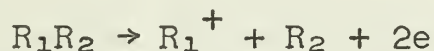
K.E. = excess kinetic energy in the process, and E.E. = excitation energy (electronic, vibrational, or rotational) which the ion or neutral fragment may possess.

If the formation of negative ions is considered, then two additional dissociative mechanisms must not be excluded. All three can be summarized as follows:

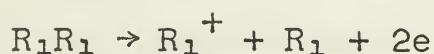
- (1) $AB + e \rightarrow A^+ + 2e$; $A.P.(A^+) = D(AB) + I(A) + E.E. + K.E.$
- (2) $AB + e \rightarrow A^+ + B^- + e$; $A.P.(A^+) = A.P.(B^-) = D(AB) + I(A) - E.A.(B) + E.E. + K.E.$
- (3) $AB + e \rightarrow A + B^-$; $A.P.(B^-) = D(AB) - E.A.(B) + E.E. + K.E.$

A.P., the appearance potential of an ion is defined operationally as the minimum energy of the bombarding electrons at which the fragment ion can be detected. I is the ionization potential of a given fragment, and E.A., the electron affinity of a given fragment.

Occasionally, however, all data cannot be ascertained directly, and recourse must be made to an indirect method which incorporates thermochemical values calculated or obtained by other means. Under this circumstance, the appearance potential of a fragment is measured from two separate processes:



$$(1) \quad \Delta H_f (R_1^+) = A.P. (R_1^+) - \Delta H_f (R_2) + \Delta H_f (R_1R_2)$$



$$(2) \quad \Delta H_f (R_1) = A.P. (R_1^+) - \Delta H_f (R_1^+) + \Delta H_f (R_1R_1)$$

$$\text{From (1): } D(R_1-R_2) = A.P. (R_1^+) - \Delta H_f (R_1^+) - \Delta H_f (R_1)$$

$$\text{since } I (R_1) = \Delta H_f (R_1^+) - \Delta H_f (R_1)$$

EXPERIMENTAL METHODS FOR DETERMINING APPEARANCE AND IONIZATION POTENTIALS

In principle, the method consists of measuring the intensity of the ion current of a fragment as a function of the accelerating potential of the electron beam. In order to minimize instrumental and experimental errors, a noble gas is added and the voltage scale is calibrated with respect to the gas whose ionization potential is known from spectroscopic measurements. The electron voltage at which the ion current just vanishes is then, by definition, the appearance potential (vanishing current method). Due to the subjectivity involved in this approach, an alternate method, the linear extrapolation method, has also been used wherein linear portions of the curves are extrapolated to zero ion current. Warren (1) attempted to eliminate subjectivity by introducing the extrapolated differences method, suggesting that extrapolation of the voltage difference between points of equal ion current to zero affords a more precise measure of the appearance potential.

Although other methods have been devised, none were proven to be completely satisfactory until the advent of the retarding potential difference (RPD) method which overcame a major obstacle, the tailing phenomenon, the uncertainty at which the appearance potential curve approaches the voltage axis. Utilizing pseudo-monoenergetic electrons, Fox (2) has demonstrated that a plot of the difference in ion current due to a retarding potential as a function of the ion current results in a straight line. This can then be unambiguously extrapolated to zero current.

MEASUREMENT OF KINETIC AND EXCITATION ENERGY

In most experimental data, the excess energy of fragment ions have been assumed to be negligible, reference often being made to an empirical observation, Stevenson's Rule (3), where $A.P. = D(R_1-R_2) + I(R_1)$ if $I(R_1) < I(R_2)$. If $I(R_1) > I(R_2)$, then the neutral product is produced with excitation energy.

Two general methods are distinguishable:

(1) Those involving the use of retarding potentials such as the quantitative method of Hagstrum (4), who determined initial kinetic energy distributions of fragment ions produced in the ionization of CO, N₂, NO, and O₂.

(2) Those based upon the fact that the focusing properties of mass spectrometers depend upon the amount of kinetic energy with which an ion is formed. This is exemplified in the method of Warren and McDowell (5), in which the ion current is examined as a function of the ion accelerating potential.

In general, ions produced in simple processes have no kinetic energy, whereas excess energy is often associated with ions whose appearance potential curves show greater tailing than those of rare gases.

ELECTRON IMPACT STUDIES OF ORGANOMETALLIC COMPOUNDS

Metal cyclopentadienyls. The average bond dissociation energy for a series of metal cyclopentadienyls (6) suggest that the nature of the metal-ring bond in Mn(C₅H₅)₂ and Mg(C₅H₅)₂ is different from the others. For a group of substituted ferrocenes, the dissociation energy of the unsubstituted ring is greater than that of the substituted (7). Furthermore, the large abundance of Mn(C₅H₅)⁺ in the mass spectrum of benzene (cyclopentadienyl) manganese (8) and the virtual inexistence of Mn(C₆H₆)⁺ implies that $D(Mn-C_5H_5) > D(Mn-C_6H_6)$.

Metal carbonyls. The stepwise loss of CO in the dissociation of the molecular ion is characteristic of all metal carbonyls investigated (9-12). The ionization potentials of these ions suggest that the ionizing electron is removed from an orbital essentially localized on the metal atom. In the polymetallic carbonyls, the presence of bare metal ion clusters indicates that qualitatively, M-CO bonds are weaker than M-M bonds. Although thermochemical data have been compiled for many dissociation fragments, bond energy values have not usually been determined because of evidence supporting the presence of excess energy. The Cr⁺ ion, for example, is thought to be formed in a d⁵ (²I_{11/2}) excited state.

Metal carbonyl derivatives. For the isoelectronic series, C₅H₅Co(CO)₂, C₅H₅Mn(CO)₃, and C₅H₅V(CO)₄, C₅H₅M⁺ ions were most abundant in the spectrum, indicating that the M-C₅H₅ bond is stronger than the M-CO bond. In a nitrosyl, C₅H₅Mo(CO)₂NO (1^a), CO is lost

preferentially to NO or C₅H₅ and the presence of Mo(C₅H₅)⁺ and absence of MoNO⁺ suggest that the Mo-C₅H₅ bond is the most resistant to cleavage. Metal cyclopentadienyl bonds are also thought to be stronger than M-M bonds as observed in the spectrum of (C₅H₅FeCO)₄ (15). On the other hand, the high stability of M-M bonds relative to M-CO bonds, as in the polymetallic carbonyls, is further substantiated by the fragmentation of ClCCo₃(CO)₉ and CH₃CCo₃(CO)₉ (12). Thus in general, D (M-C₅H₅) > D (M-M) > D (M-CO).

Group IV hydrides and their alkyl derivatives. The present data on group IV hydrides (16a) is unsatisfactory in that large discrepancies in thermochemical values exist, especially if the process involved is one of extensive fragmentation (e.g. Si⁺, Ge⁺, GeH⁺). However, greater reliance may be placed on the data compiled on ions formed in less extensive dissociative processes (e.g. SiH₂⁺, SiH₃⁺).

Whereas the average C-H bond energy, E (C-H) in methane is comparable to the dissociation energy of the first C-H bond, D (CH₃-H), this is not the case in SiH₄. This anomaly is even more marked when the C-C and Si-Si dissociation energies in ethane and disilane are compared. Trimethylsilane derivatives also conform to this observation, although four sets of data have been proposed for D ((CH₃)₃Si-X) (16 a,b,c). In other words, the dissociation energy of the Si-Si bond appears to be greater than one would predict by means of the principle of constant bond energies throughout a series of apparently similar compounds. Furthermore, for a group of mono-alkyl derivatives Si-C bond energies have been shown to be comparable to C-C dissociation energies (16 d).

A constant difference of D minus E of 20-21 kcal./mole among a group of substituted trimethylstannanes (17) led to the association of this quantity with the "reorganization energy" of the Sn(CH₃)₃ radical. This value is doubled in Sn₂(CH₃)₆, for which the reorganization must occur twice during the rupture of the Sn-Sn bond.

Silylphosphine and silylgermane. The Si-P dissociation energy of silylphosphine is greater than either D (H₃Si-SiH₃) or D H₂P-PH₂ as expected from the differences in electronegativities of the SiH₃ and PH₂ radicals (18). However, the increased stability of the Si-Ge bond in silylgermane relative to Si₂H₆ and Ge₂H₆ cannot be rationalized by analogy (19). Nevertheless, this result is not unexpected if (d→d)π interactions are predominant in silylgermane.

The examination of electron impact phenomena in organometallic chemistry has also encompassed various other compounds including organolithiums (20), boron hydrides (21,22), group V hydrides (23) and mercury, zinc (24), and beryllium (25) alkyls.

Despite the considerable body of self-consistent and generally reliable thermochemical data that have been accumulated from mass spectral research, inconsistencies exist and these will have to be resolved. Moreover, the necessity for more efficient and precise experimental methods, especially in determining excess energies, is

evident. Many possibilities can be foreseen, nevertheless, with over 200 prospective compounds (26) for the mass spectrometer.

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RECENT ADVANCES IN CARBORANE CHEMISTRY

Robert Lawrence

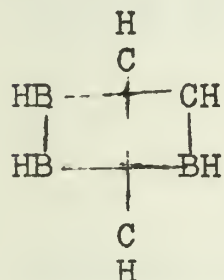
December 15, 1966

INTRODUCTION

Many advances have been made in carborane chemistry in recent years. Carboranes of the general formula, $C_n B_m H_{m+n}$, have been prepared for all cases of $n=2$ and $m=3-10$. In addition, derivatives of one-, three-, and four-carbon carboranes and a number of hydrocarboranes have been recently reported. Although, strictly speaking, only those cases in which the number of hydrogens $= n + m$ (and there are no bridge hydrogens) are considered true carboranes, any system of C-B-H in which the carbon atoms and boron atoms make up an integral part of a polyhedral or near polyhedral framework is loosely considered as a carborane.

NOMENCLATURE

According to the unofficial rules of the Nomenclature Committee of the Inorganic Division of the A.C.S., carboranes are named as is illustrated in the following example:



is called 1, 2-dicarboclovohexaborane (6).

"Dicarba" indicates that there are two carbons within the framework. "Clovo" indicates that the structure is a closed cage and is used only in those carboranes in which the cage is complete. "Hexaborane" indicates that the carborane has a total of six carbons and borons in the framework; the concluding, "(6)", indicates that there are six hydrogens in the unsubstituted compound. The numbering system follows the convention of numbering an apex, then the belt atoms, and finally, the opposite apex (1).

PREPARATION AND STRUCTURES OF THE CARBORANES

The smaller carboranes-- $C_2B_3H_5$, 1, 2- $C_2B_4H_6$, 1, 6- $C_2B_4H_6$, and $C_2B_5H_7$ --have been prepared by reactions--electrical, thermal, or photolytic--of acetylene and diborane or pentaborane or by the decomposition of intermediates obtained by these methods. Table I summarizes these methods.

Table I

Starting Materials	Method	Products	Structure	Ref.
1) $RC \equiv CR', B_5H_9$ $C_2B_4H_8$	silent electric discharge	$C_2B_4H_8$ $1,5-C_2B_3H_5$	----- trigonal bi-pyramid	2,3,4
2) B_2H_6, C_2H_2	silent electric discharge isolated by vapor phase chromatography	$C,3-Me_2-$ $1,2-C_2B_3H_3$	" " "	5
3) 2-butyne, B_5H_9	pyrolyzed with Me_3N	$1,6-C_2B_4H_6,$ $C_2B_5H_7$	octahedron pentagonal bipyramid	4,6 12
4) $C_2B_4H_8$	silent electric discharge	$1,2-C_2B_4H_6$		3
5) $C_2B_4H_8$	photolyzed	$1,2-C_2B_4H_6,$ $1,6-C_2B_4H_6,$ $C_2B_3H_5$		7
6) B_2H_6, C_2H_2	electrical flash discharge	$1,2-C_2B_3H_5,$ $1,2-C_2B_3H_5,$ $1,6-C_2B_4H_6,$ $2,4-C_2B_4H_6$ also mono- and dimethyl derivatives		8

The structure of the dihydrocarborane, $C_2B_4H_8$, is interesting in that this compound differs considerably in structure from its "parent" carborane. The 12.8-Me. ^{11}B mnr of C-alkylated derivatives of the compound show three boron environments in the ratio of 1:2:1 (9). The pentagonal pyramid with two bridge hydrogens, indicated by this evidence, is confirmed by a single crystal X-ray study by Lipscomb (10,11).

While mixtures of all the carboranes with $n=2$ and $m=3-5$ or their derivatives are prepared by discharges through acetylenes and diborane or pentaborane, more specialized methods are needed to prepare the heavier carboranes. A derivative of $C_2B_6H_8$ was obtained by Williams and Gerhart, who irradiated a mixture of $(CH_3)_2C_2$ and B_6H_{10} with ultraviolet at high temperatures to obtain $(CH_3)_2C_2B_6H_8$ in moderate yield. A distorted Archimedean antiprism was indicated as the structure by ^{11}B mnr (13).

Carborane, $C_2B_{10}H_{12}$ is obtained in good yields by reacting acetylene with $B_{10}H_{12}(SEt_2)_2$ or $B_{10}H_{14}$ in the presence of base (4). Numerous X-ray studies of carborane or its derivatives, such as the study of $B_{10}Cl_8H_2C_2H_2$ by Lipscomb, have shown the compound to be an only slightly distorted icosahedron (14,15).

Year	Month	Day	Event	Location
1930	Jan	1	First meeting of the committee	London
1930	Feb	15	Second meeting of the committee	London
1930	Mar	1	Third meeting of the committee	London
1930	Apr	15	Fourth meeting of the committee	London
1930	May	1	Fifth meeting of the committee	London
1930	Jun	15	Sixth meeting of the committee	London
1930	Jul	1	Seventh meeting of the committee	London
1930	Aug	15	Eighth meeting of the committee	London
1930	Sep	1	Ninth meeting of the committee	London
1930	Oct	15	Tenth meeting of the committee	London
1930	Nov	1	Eleventh meeting of the committee	London
1930	Dec	15	Twelfth meeting of the committee	London

The following is a list of the members of the committee who attended the meetings during the year 1930. The names are given in alphabetical order of their surnames.

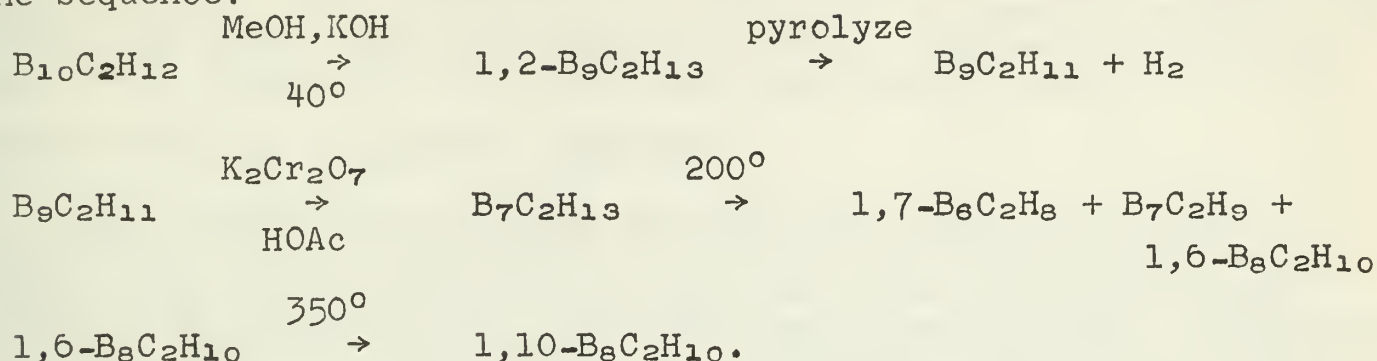
Mr. A. B. C. D. E. F. G. H. I. J. K. L. M. N. O. P. Q. R. S. T. U. V. W. X. Y. Z.

The committee met on the following dates: 1st Jan, 15th Feb, 1st Mar, 15th Apr, 1st May, 15th Jun, 1st Jul, 15th Aug, 1st Sep, 15th Oct, 1st Nov, 15th Dec.

The committee met at the following locations: London, London, London, London, London, London, London, London, London, London, London, London.

The committee met for the following purposes: First meeting of the committee, Second meeting of the committee, Third meeting of the committee, Fourth meeting of the committee, Fifth meeting of the committee, Sixth meeting of the committee, Seventh meeting of the committee, Eighth meeting of the committee, Ninth meeting of the committee, Tenth meeting of the committee, Eleventh meeting of the committee, Twelfth meeting of the committee.

Hawthorne has worked out a route of obtaining B_8 -- B_9 carboranes by successive degradation of carborane. These degradations follow the sequence:



^{11}B nmr and other evidence indicate the following structures:

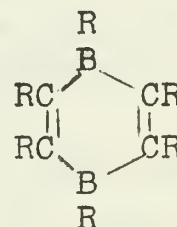
$C_2B_8H_8$ --Archimedean antiprism, $C_2B_7H_9$ --tricapped trigonal prism, $C_2B_8H_{10}$ --bicapped Archimedean antiprism (16,17,18,19).

In addition to the above two-carbon carboranes there have been reported carboranes or derivatives of carboranes containing one, three, and four carbon atoms. Onak and co-workers identified a product of the electric discharge of 1-methylpentaborane as monocarbahexaborane (7) on the basis of ^{11}B nmr and other evidence (20). Spielman and Williams isolated a derivative of a carborane identified as CB_5H_9 --a pentagonal pyramid. The product was obtained from the thermal reaction of acetylene and pentaborane (21).

Todd and co-workers reported the synthesis of $B_{10}CH_{13}^-$ derivatives by reaction of decaborane with alkyl isocyanides. Spectral data indicate a structure whose framework is similar to Hawthorne's carbollide (22).

Bramlett and Grimes obtained derivatives of $C_3B_3H_7$, whose ^{11}B nmr indicates a pentagonal pyramidal structure (23).

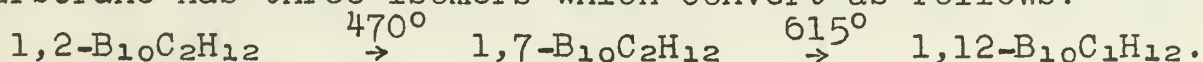
Binger reported from the attempted synthesis of



a compound which instead--because of its high stability, its lack of a double bond, and its nmr--appeared to be a derivative of the carborane, $C_4B_2H_6$, with octahedral structure (24).

STRUCTURAL ISOMERISM OF CARBORANES

In all carboranes reported, structural isomerism is possible. Carborane has three isomers which convert as follows:



On the basis of molecular orbital calculations, carboranes with adjacent carbon atoms are unstable with respect to all other structural isomers (26). This is quite well borne out by chemical evidence, as it is seen that almost all carboranes either form with nonadjacent carbons or revert to such structures upon being heated.

SUMMARY OF SOME DERIVATIVE CHEMISTRY

Much derivative chemistry of carboranes has been reported. Hartwell has already discussed the silicon and phosphorous derivatives (4). Sulfur derivatives (27), amine derivatives (28,29), metallic derivatives (30), and others have been prepared. Hawthorne, realizing that the exposed face of the $B_9C_2H_{11}^{-2}$ structure should be isoelectronic and isoorbital with $C_5H_5^-$, prepared such compounds as $\pi C_5H_5 Fe(\pi B_9C_2H_{11})$ (31), $(B_9C_2H_{11}) Re(CO)_3^-$ (32), and several related compounds.

POSSIBLE USES OF CARBORANES

Many practical uses of carboranes are possible. These include inorganic polymers, many of which have already been reported (e.g., 33), and chemotherapeutic work against cancer. Carboranes are very stable and physiologically inactive, but they are rich in the isotope ^{10}B (about 20% of naturally occurring boron) which absorbs harmless slow neutrons and give off weak α particles and 7Li . The α particle is of low enough energy to destroy only tissue in its immediate vicinity. Unlike the stable boranes ($B_{12}H_{12}^{-2}$), carboranes have carbon atoms which can act as "handles" for groups such as $-SH$ by which the compound can be made to attach itself to tumorous tissue.

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"NMR Investigations of Some Metal Alkoxide Systems"

L. L. Murrell

December 20, 1966

Structural investigations of metal alkoxides have received considerable attention in the past decade. A 1964 seminar (1) summarizes the subject up to that time. Surprisingly, n.m.r. was not used in investigations of metal alkoxide systems before 1962. Trimethylsiloxides of gallium and aluminum were reported to be dimeric on the basis of n.m.r. investigations (1). Several recent papers have exemplified the power of n.m.r. in structural determinations of metal alkoxide and, also, as a unique technique for investigating the chemical stability of species in solution.

Often solid state and solution structures are quite different. For example, dimethyl gallium hydroxide and ethyl titanate are tetrameric in the solid state (2,3) but are trimeric in solution. In such cases, n.m.r. may yield unique information.

Shiner, Wittaker, and Fernandez (3) investigated aluminum t-butoxide and aluminum isopropoxide in a number of solvents using n.m.r. spectroscopy. Investigation of $\text{Al}(\text{OBu}^t)_3$ confirmed Bains (5) observation that two distinguishable t-butoxide groups exist in dimeric aluminum t-butoxide. The n.m.r. investigation of aluminum isopropoxide in a number of solvents (4) led to an assignment of structure in agreement with that proposed by Bradley (6).

Freshly distilled aluminum isopropoxide has a trimeric structure (7) which, upon standing, slowly crystallizes to the tetrameric form. The n.m.r. spectrum of the molten trimeric structure was investigated. A temperature dependent n.m.r. spectrum was observed for trimeric aluminum isopropoxide in a number of solvents, and possible structure and mechanisms were discussed.

Van Wazer and Weingarten (8) assigned the structure of tetramethyl titanate and tetraethyl titanate using n.m.r. The n.m.r. spectrum of tetramethyl titanate was consistent with the crystalline ethyl titanate structure (3). The structure assigned to trimeric ethyl titanate was that proposed earlier by Martin and Winter (9).

No coordination complexes resulting from the union of a neutral molecule and a metal alkoxide were reported prior to 1951, and only a handful of stable transition metal alkoxide complexes have been reported since that time. In 1962, Bains and Bradley (10,11) published two papers concerning coordination complexes of metal alkoxides with hydrazine and ethylenediamine, respectively. Aluminum isopropoxide hydrazinate, $\text{Al}(\text{OPr}^i)_3 \cdot \text{N}_2\text{H}_4$, and aluminum isopropoxide hemihydrazinate, $\text{Al}(\text{OPr}^i)_3 \cdot 1/2 \text{N}_2\text{H}_4$, were the only aluminum hydrazine complexes reported to exist from analytical evidence. Aluminum t-butoxide did not form a stable complex with hydrazine. Only one aluminum alkoxide ethylenediamine complex was isolated by Bains and Bradley; namely, the binuclear complex $[\text{Al}_2(\text{OPr}^i)_6 \cdot \text{en}]$. Several possible structures were proposed for this complex.

Shiner and Wittaker (12) studied aluminum isopropoxide ethylenediamine and t-butoxide ethylenediamine complexes using n.m.r. techniques. They reported a concentration-dependent, temperature-dependent study of $[Al_2(OPr^i)_6 \cdot en]$ in a number of solvents. Only the conclusions of Shiner and Wittaker's n.m.r. study will be included here:

- 1.) Intramolecular exchange of isopropyl groups is fast, except at -62° based on broadening of the methyl proton peaks.
- 2.) Intermolecular exchange of complexed and excess ethylenediamine is slowed on cooling to -18° in the absence of isopropyl alcohol, but is fast even at -62° in the presence of excess isopropyl alcohol.
- 3.) Intermolecular exchange between complexed and uncomplexed isopropyl alcohol is slow below 0° in the presence of excess ethylenediamine. The authors made a structural assignment based on the details of their n.m.r. data. The aluminum t-butoxide complex was too unstable to investigate in detail.

Future work on metal alkoxide compounds and their reactions will undoubtedly use n.m.r. as a fundamental tool. Some systems that have not been investigated using n.m.r. are: $[TiCl(Obu)_3]_3$, $[TiCl_2(Obu)_2]_2$, $[Ta(OR)_5]_2$, $Ta(OR)_5 \cdot ROH$, $[Al(OEt)_3]_4$, $[Al(Obu^i)_3]_4$, $[Al(OsecBu)_3]_2$, $[B(OMe)_3]_2 \cdot en$, $[B(OPr)(OMe)_2] \cdot en$, $Zr(OPr^i)_4 \cdot Pr^iOH$, $Zr(OPr^i)_4 \cdot NC_5H_5$.

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HOMOGENEOUS CATALYSIS OF ISOMERIZATION AND SPECIFIC HYDROGENATION OF OLEFINS

Hassan A. Tayim

January 3, 1967

Homogeneous catalysis has been only recently recognized as a possible route to the understanding of heterogeneous catalysis. The general subject of homogeneous catalysis has been regularly reviewed by Halpern since 1956 (1-5).

It has been recently reported that systems of the type $MX_2(R_3Q)_2 + M'X_2$ where R = phenyl or alkyl group, Q = P, As, Sb; M = Pt, Pd, Ni; M' = Pb, Sn, Ge; X = Cl, I, Br, C $\sqrt{}$ catalyze the high pressure hydrogenation of soybean oil methyl esters to the monoene (6). The reaction does not proceed to complete saturation. Hydrogenation of butadiene to butene has been effected by cobalt(II) pentacyano ion as a catalyst (7).

The present work is an attempt to test the generality of these findings and to elucidate the mechanisms of the reactions involved.

All the polyolefins investigated, with the exception of those having aromatic or semiaromatic character, were catalytically hydrogenated to the monoenes. Under relatively mild reaction conditions, only isomerization of the olefins could be effected. The list of catalysts was extended to include complexes of the above type with the ligand R_2Q , where Q = S, Se, and complexes of the type $MX_2(\text{diolefin})$.

The role of the cocatalyst $M'X_2$ has been investigated and compounds of the type $M'X$ where M' = Tl, In, Ga; $M'X_3$ where M' = Bi, Sb, As, P and carbon monoxide were compared. Tin(II) chloride has been found to be most effective in activating the catalysts. It is suggested that, in the presence of chloride ions in solution, this cocatalyst functions through its complex ion $SnCl_3^-$ which is known to be a strong π -acceptor (8).

The effect of the solvent, the nature of the olefin, the nature of the catalyst and other related factors have been studied.

A plausible mechanism of the hydrogenation reaction consists of a fast isomerization of the polyolefin to the conjugated isomer by stepwise migration of the double bonds, followed by a slow hydrogenation of the conjugated olefin to yield the monoene. The olefin undergoes isomerization and/or hydrogenation while coordinated to the central atom of the catalyst. A metal hydride complex formation is an essential step in this mechanism. Evidence for the mechanism is obtained from analysis of the isolated intermediates (both organic compounds and organometallic complexes) and from kinetic studies.

Parallelism to heterogeneous systems is suggested. The activation of platinum catalysts effected through platinum-tin bonding when the catalytic system includes tin(II) chloride as a cocatalyst can be compared to the activation of a nickel catalyst brought about by electronic interaction of nickel with germanium when a germanium support is used (9).

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NUCLEAR-ELECTRON DOUBLE RESONANCE

THE OVERHAUSER EFFECT

L. G. Kent

February 14, 1967

I. Subject and Synonyms:

The Overhauser Effect (OHE)

Dynamic Nuclear Polarization

Nuclear-Electron (and Nuclear-Nuclear) Double Resonance

II. Nature of the Effect:

In NMR Double-resonance experiments three effects appear:

- 1) Perturbation of individual spin systems by the second RF field, causing state-mixing, hence transitions not present in single resonance systems. Minimized by spreading levels (increase field; vary sample).
- 2) Nuclear Stirring: the effect of strong RF fields on mean lifetimes in excited states. Such competitors to OHE are minimized by using low temperatures, transient (pulse) techniques, and minimum fields.
- 3) OHE, denoting perturbation of a medium-linewidth NMR system by preferential population of the excited- or ground-eigenstate of the nuclear Spin Hamiltonian. Two-spin-system description follows.

A. Mathematics of OHE:

Discussed in seminar; concise set of equations available upon request.

B. Mechanisms by which populations may be altered:

1. Active: Separate signal excites second spin, yielding OHE.

- a. Dipole (vector) interaction occurs through space. In the electron-nuclear case its magnitude is that of ESR hyperfine splitting. As expected, d-d coupling suffers an inverse cube radial dependence, and it "averages out" through molecular rotation but not through exchange (62). Particles whose magnetic moments have the same sign are enhanced positively through this mechanism when the mate is excited.
- b. Fermi (scalar) coupling is of the order of magnitude of contact shifts in NMR, suffering no predictable r-dependence. It is "averaged out" through exchange but not through rotation, except as interference with bond-anisotropy (partial multiple character) augments or diminishes it. The details of this mechanism are unknown (14).

2. Passive: Second spin excited without separate signal.

- a. "Brute Force": The lattice is cooled, a D.C. H_0 provided, and in time I reaches thermal equilibrium. $h\nu = g\mu\beta H \gtrsim kT$. $p = \tanh(\frac{1}{2}g\mu\beta/kT) \lesssim 10^{-7}$ H/T. Fields must thus be high, ca. 10^5 Gauss, and T low (ca. 0.01°K). Internal fields at nuclei of paramagnets are of this order, but temperatures are still quite low.

- b. Nuclear Spin Refrigerator: (10-11) Electrons here act as the working substance transferring heat from nucleus to bath. Cooling comes via changing energy $gm\beta H$ during portions of the cooling cycle. Methods used: vary H_0 angle; rotate sample if g is anisotropic; change g through sonic pressure change; change g electrostatically. Rate $(T_{1e})^{-1}$ is, in effect, a "switch" between electron spin and bath. Cross-relaxation represents a valve between nuclear and electron spins; to operate it one merely makes the electron spin g -factor low, lowering the electron Larmor. Nuclear R.F. hence suffices to excite, during part of the cycle, the electron Larmor. More rapid cycling overrides competing effects and yields higher polarization. 30% polarization reached to date.
 - c. Hot Conduction Electron: In semiconductors a D.C. E-field is impressed in the presence of H_0 at low temperatures. This yields a Hall-Effect voltage which is used internally to excite the electronic transition normally excited by microwaves in OHE. Enhancements of 100 have been reported for ^{123}Sb
 - d. Photon Pumping, preferentially populating the excited or ground state in a manner identical to that of optical pumping in the laser (29a), yields polarizations of about 40% to date.
- C. Accompanying Effect: Changes in relaxation times T_1 and T_2 invariably accompany OHE. This is a valuable and often used co-observable in pulsed (1,7,13,36,45,46) and non-pulsed (28, 29,48) systems. It must be emphasized that relaxation occurs only through the presence of Larmor frequency, as does any change in the orientation of the nucleus in a magnetic field. Here we shall consider only nuclei of spin $1/2$ to avoid nuclear multipolar complications. Thus relaxations occur through modulation of dipolar and scalar couplings at the Larmor frequency, and/or through the existence of a frequency component at Larmor modulating an external magnetic field. Where $I > 1/2$, quadrupolar interaction often becomes the principal relaxation mechanism. Since rotations and exchanges occur about a band of frequencies approximately Lorentzian in distribution, the existence of a component near Larmor (ca. 10 MHz) will be such as to yield relaxation times in the order of seconds for many nuclear-nuclear interactions and of hundredths of seconds for many nuclear-electron processes.

III. History: Albert W. Overhauser published his initial work on the effect in 1953 (20,21) at Berkeley and, a few months later, carried his new-found field to the U. of I., where he joined our Physics faculty. It is interesting to see that although recognition was made of the observables above, with abundant reference to simultaneous spin-flipping, energy conversion, and relaxation times, no mention was made of population inversion to explain inverted NMR signals. Yet manipulation of population levels, creating various (and even negative) spin tem-

peratures, defined thus: $\text{Pop.}^*/\text{Pop. Ground} = \exp. (-E^*/kT)$ is the key to OHE.

For decades following Einstein's mathematical hint at population inversion nothing significant was accomplished toward demonstrating it (29a). Bloch proposed the first such experiment in 1946. In 1951 Purcell and Pound produced a small stimulated emission, indicating inverted populations, or "negative spin temperature." The first significant stimulated emission was demonstrated in the mid-1950's by C. H. Townes, who actually achieved Molecular Amplification by Stimulated Emission of Radiation, to the point of self-oscillation. He utilized the inversion of NH_3 , at 22GHz; the M then stood for "Microwave." Nuclear Larmor frequency MASERS have since been produced using the OHE. Spectral stability and monochromaticity are excellent, but are several orders of magnitude inferior to Mossbauer's $1:10^{15}$ (the latter seen in the gamma region) (32,41,42). Of several good historic and tutorial references (20-29), C.D. Jeffries' (22) is recommended for initial reading; it is brief and pithy.

IV. Chemical Applications: (14,39,44,47,48,1-19)

- A. Enhancing weak NMR signals, particularly those of ^{13}C and ^{31}P , obviating the need for isotopic enrichment. This is generally accomplished by dissolving a trace of paramagnetic material in the substance under study, since the electron possesses a far greater "handle" (magnetic moment) for interaction with the nucleus in question than will any neighboring nucleus. In formed crystals or polymers, paramagnetic centers may be introduced by irradiation with gamma or X-radiation. The substance, either in solid or liquid form, may then be placed inside a microwave cavity (supplying electron Larmor) in the magnetic field, with the usual NMR crossed-coil set imbedded in the sample. Super-regenerative and marginal oscillator systems, used in wide-line NMR, are not recommended because of high stability requirements. Linewidth demands are in the order of a few Hz (12,67). A few examples in this category: Characterization of carboranes; Anisotropic effects in carbonyl crystals; isovalent hybridization and d-pi/p-pi backbonding studies of carbon-containing ligand systems; organometallic interactions (63); conformational studies in organic chemistry (high-resolution); ^{31}P as a dopant in semiconductors. Maximum theoretical enhancement ratio = $|\chi_e/\chi_n|$.
- B. The study of correlation (influence, or "sticking") times in liquid solution (5,6,52,30) centers about the relationship between the d-d and scalar mechanisms. Polymerization studies, casual-bond strength, and kinetics investigations appear to be the most promising areas under this caption.
- C. Detection of scalar coupling between R• electron and solvent nuclei: How easily are electrons on the solvent molecule unpaired? Polymerization potential includes this and geometric factors. Hyperconjugated and conjugated systems, and the energy of electron-promotion into a multiplicity-forbidden state; pi-, mu-, and delta- bonding in light of the ease of such e^- promotion into a higher, unused orbital; study of the yet un-

known scalar interaction mechanism (4,9,14,36,40,44,48,52-4); anisotropy of the scalar interaction--partial π -character; crystal lattice forces (8,9,61,62); geometric relationship of delocalized e^- 's to H_0 and to individual atoms, via multiple-spin experiments (7,45). In line with this: investigation of geometry and mechanism of heterogeneous catalysis.

D. Role of e^- 's and dopants in semiconduction (33,35,38,66): the Hall effect; anisotropy and conductivity mechanisms in metals (34,38,43).

E. Orientation of nuclei by application of an X-degree-long Larmor pulse to cause nuclei to shift X^0 from the Z (H_0)-axis, manifesting itself in reorientation of anisotropic α , β and γ emissions, related both to nuclear and, apparently, to electronic position (9,47).

F. Study of nature and effects of ferro- and antiferromagnetism, and superconduction both in conductors and semiconductors (3).

G. Relaxation mechanisms and linewidth in NMR; T_1 and T_2 in their separate roles (9,27,37,44,48).

V. Equipment: The following are necessary modifications of ordinary high-resolution systems. H_0 must be stable and usable over the range 1-5000 Gauss or more. Though sensitivity is approximately proportional to the cube of the frequency, lower fields are economical; they allow superior stability of the electron Larmor and of the system under pulsed conditions; more electron Larmor power is available because of transmitter and field transducer; and more power can be absorbed due to increased skin depth (24). Low temperature work yields the usual advantages seen in ordinary NMR, plus that of narrowed electron Larmor width, hence greater ease of saturation. Facility must be added for pulsing and varying continuously the amplitudes and frequencies of both (all) RF and microwave drives. Rotation of sample may be desirable, as may electronic rotation of H_0 . Little Larmor power is required, especially when driving forbidden transitions, most popular because these perturb the rest of the system least, hence give fewest spurious signals.

VI. The Field Today: OHE, relatively young, is beset by a minimum of "infinite-refinement-of-technique." Investigations are still being made into the basic governing equations--rate, polarization, and scalar spin interaction. Three-spin effects (7,45) with R. dissolved in ϕF_6 , ϕH_6 , and ϕF_3H_3 reveal alternate paths of spin-spin interaction. Pulsing shows the time-dependent roles of d-d and scalar coupling. Nuclear relaxation times are studied by Försen (17) in a manner analogous to that used in NMR exchange studies. The Phonon Bottleneck (9) was felt first through anomalous electron Larmor power requirements and polarization buildup rates. It appears that this acoustic phonon, the one mechanical link between nucleus and lattice, when unable to carry off all the required nuclear energy, is responsible for converting Larmor to heat. Richards (1,2) in studying ^{13}C and ^{31}P enhancement, indicate inferior enhancement at higher fields, and suggest a decrease in electron correlation as the cause; he finds, too, that pentavalent

P is less subject to OHE enhancement than is trivalent, suggesting scalar action through unshared pair. Large halogens are cited as particularly capable of transmitting OHE (4,6). Relationships of microwave power required, absorption shape, relaxation times, radical, and gyromagnetic ratio are studied attendant to the assignment of weighting factors to the main models considered in scalar coupling: the STICKING, SHELL-OF-INFLUENCE, and DIFFUSION models (5,6,8,22,53). Partial-double-bond breaking on rotation of t-butyl groups and slow relaxation compared to exchange in the (t-bu)₃ O-OH offer explanation for anomalous sign and degree of scalar coupling (3,6). Rough allusions are made to the content of each reference following its listing in the original draft; this is available on request.

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VI. Glossary of Terms Used in This Seminar and Throughout the Literature:

A, b:	Empirical constants
D:	Polarization diffusion time, in sec. cm^{-2} . $\langle D \rangle$ = expectation value of D.
g:	Lande factor: 2.00 for free electron; 0.003 for nuclei discussed.
H ₀ :	Field (Gauss) seen by spin under consideration, subscripted if not uniform.
\vec{I}, \vec{S} :	Spin vectors (electron's always \vec{S}); I_z : Z-component: integer or 1/2-integer.
J _d (0):	Dipolar spectral density at Larmor ($\omega \rightarrow 0$), a near-Lorentzian function.
j _e :	Normalized ($J_e = J_{\text{scalar}}$) = $J_e(\omega)/J_e(0)$.
N:	Nr. paramagnetic moieties cm.^{-3} ; n, n': Nr. of observed nuclei cm.^{-3} .
P:	Nuclear polarization; p: electronic; $\dot{P} \equiv P' \equiv dP/d(t=\text{time})$.
T _{1e} :	Electron spin-lattice relax'n. time; longitudinal ($\parallel H_0$) relax'n. time.
T ₂ :	Dipole-dipole (d-d) rel. time; transverse ($\perp H_0$) relaxation time.
W, w, U, u:	Transition probability: Capital = nuclear; U = transverse; i = forbidden.
β :	Bohr magneton: value for electron used in all equations.
γ :	Magnetogyric (gyromagnetic) ratio, = (ν/H_0).
δ :	Dipolar effect, = $\gamma_e (\hbar \gamma_I \chi_S b^{-3})^2$.
ξ :	$J_e(0)/J_d(0)$ = scalar density/vector density (dipole-dipole).
H _m :	Motional Hamiltonian; H' = OHE (i.e. spin-spin) H: a perturbation H.
$\omega_e \equiv \omega_s$:	Larmor frequency of electron, Hertz; ω_e = the same, in radians/sec.
τ, t :	Time; c: correlatiin ("sticking") or influence; ex or e: exchange.
σ/ρ :	OHE enhancement, denoted in Solomon's modification of the Bloch equations.

MOLECULAR BEAMS

G. A. Lasby

February 21, 1967

Introduction

Molecular beams have been very important in the experimental verification of some of the "postulates" of the kinetic theory of gases and of quantum mechanics.^{1,2} They have also been very important in the field of spectroscopy¹ as a source that does not suffer from Doppler broadening and as an instrument for the accurate measurement of nuclear properties.² Probably their most exciting present use is in the investigation of collision phenomena.^{1,3,4}

There are a number of good reviews^{1,2,3,4} of molecular beams. The best of these for the beginner is K. F. Smith's Molecular Beams, in that the mathematical requirements are least and it is the most general.

Before considering the application of molecular beams and the results obtained from experiments, it is well to consider aspects of the experimental set up which limit application of the method. For references to the original literature, see the books by Smith, Ramsey, and Ross. Ramsey's Molecular Beams also contains a very good section on the design and use of molecular beam apparatus.

The Source

The source is essentially a container of molecules with an opening (the slit) maintained at a pressure and temperature such that the mean free path of the molecules within the source is about the same as the width of the slit. This insures that the molecules leave the source via molecular effusion rather than hydrodynamic flow. This is important because when hydrodynamic flow occurs, a cloud of molecules forms in front of the slit. This cloud then appears to be the slit. This results in a very ill-defined beam.

There are several other specialized methods of producing beams.¹ Of these, the use of a supersonic "wind tunnel"⁵ is most promising since it provides an intensity one hundred to one thousand times greater than that obtained via molecular effusion. Its use, however, is limited due to cost and the difficulty in predicting the shape and velocity distribution of the beam.

The Detector

For detection of permanent gases, a modified Pirani gage is used. When a beam of molecules falls on its entrance slit, the pressure within the gage rises, more heat is removed from the platinum filament and its temperature and resistance drop. Beam fluxes on the order of 10^{12} molecules/cm² sec can be measured.

If the beam contains an easily ionized substance, when it falls on a hot tungsten wire, the substance is ionized. These ions are then collected

by a negatively charged plate and the positive ion current measured. A flux of 10^4 molecules/cm² sec can be measured.

When used with an electron multiplier positive ion detector, bombardment of the molecular beam with energetic electrons and analysis of the resulting ions with a simple mass spectrometer is fairly effective.

There are many other more specialized techniques.

To understand the applications of molecular beams, one must know the nature of the forces tending to deflect the beam. Since the molecules are electrically neutral, electric and magnetic fields, as such, do not deflect the beam. However the molecules do have electric and magnetic dipoles, and these do interact with the gradient of electric and magnetic fields to produce a deflection. The deflections due to the interaction of the magnetic moments of the molecules are easily understood in terms of the vector model of the atom. The electrostatic interactions are much harder to understand. This is due to the polarizability of the molecule and the fact that the effective permanent dipole moment is related to the rotational state of the molecule.

There are three basic types of experiments. The simplest of these involves measurement of the actual displacement of the beam.^{1,2} This method is severely limited by the difficulty in the accurate measurement of the gradient of the magnetic field and also by overlapping of different components of the beam.

In a closely related technique,⁶ the gradients of electric and magnetic fields are varied until one component of the beam is not deflected while the others are.

The resonance method^{1,2} is in many respects similar to spectroscopy. In spectroscopy a sample is placed in a beam of light and the decrease in the intensity of the light noted. With the resonance method, "light" falls on the sample and some of the sample "disappears." This is accomplished by an arrangement of magnets and a slit such that one component of the beam falls on the detector. When the molecules in the beam component undergo a transition they no longer fall on the detector and consequently the intensity of the beam decreases.

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Chemistry and Structure of Allyl Complexes

Donald L. Tibbetts

February 28, 1967

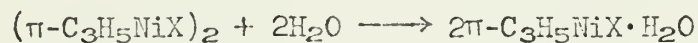
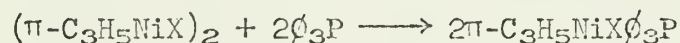
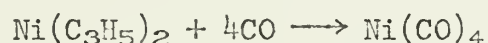
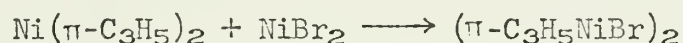
Introduction

The area of chemistry to be considered in this seminar is σ -allyl (σ -C₃H₅) and π -allyl (π -C₃H₅) complexes.^{1,2} In the σ -allyl complexes there is a classical carbon-metal bond. σ -C₃H₅MgBr is probably the best characterized compound of this type.³ Other examples are (σ -C₃H₅)₂Zn and LiC₃H₅. In the π -allyl complexes the bonding to the metal is similar to that in the metallocenes. An X-ray structure for (π -C₃H₅PdCl)₂⁴ shows the plane containing the π -allyl system approximately perpendicular to the Pd₂Cl₂ plane as in sandwich compounds. Most transition metal complexes so far synthesized are π -bonded.

Descriptive Chemistry

The pure allyl complexes of most transition metals have been synthesized from a metal halide and C₃H₅MgBr.⁵ A notable exception is the manganese compound. Why this compound can not be synthesized remains obscure. It may be associated with the tendency of Mn²⁺ to form ionic bonds as in the cyclopentadienyl complex. The complexes are air and water sensitive; most are very sensitive. Thermal stability generally increases from left to right across the periodic chart, nickel and palladium compounds being especially stable.

Because of this stability, nickel and palladium allyl complexes have been widely investigated.^{1,2,5,6,7,8} Typical reactions are:



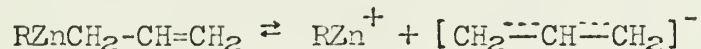
(C₃H₅)₂Pd undergoes similar reactions except where a metal carbonyl is a product.

Physical Methods

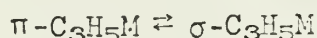
Infrared: The carbon carbon stretching mode of the σ -allyl is generally found around 1600 cm⁻¹, that of the π -allyl group around 1460 cm⁻¹.^{1,5} These bands are quite intense and provide a convenient aid in assigning structures. Unfortunately the decomposition products of an allylic complex are σ -bonded. This could cause confusion.

Dipole Moment: $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2^{9,10,11,12}$ has a symmetric structure which should have a zero dipole moment yet in benzene $\mu = 2.08$ Debye. This could be attributed to dissociation or distortion in solution or to a poor estimate of the atomic polarization.

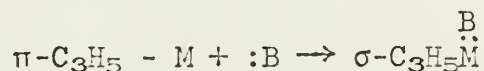
Nmr: $(\sigma\text{-C}_3\text{H}_5)_2\text{Zn}^{13}$ has an AX_4 spectrum. Thus the terminal CH_2 's are equivalent. This can be explained by a rapid exchange of the type



π -allyl groups give a AM_2X_2 spectra as would be expected.⁷ At elevated temperatures the spectra change to an AX_4 type.^{15,16} This can be explained by the following equilibrium



A great deal of speculation has been aroused by this phenomenon.^{14,17,18} Exactly what stabilizes the σ -bonded state is not known. The addition of a solvent molecule to the complex is likely. π -allylic complexes will generally undergo the reaction



A solvent participation of this type would explain the data, but is only of a speculative nature.

Conclusion

By using Nmr and IR as tools, structure elucidation of allyl compounds can be relatively straightforward. Presently a large amount of synthetic work is yet to be done, especially with the 2nd and 3rd row transition elements. The system is comparatively simple and could be a fruitful area for research.

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MASS SPECTROMETRY OF BORON HYDRIDES

John Moran

March 7, 1967

Introduction

Mass spectrometry is a tool with many advantages for the chemist. It can often provide insight into the structure of a new compound via its fragmentation pattern. Mass spectral studies may yield thermodynamic information, i.e. bond strengths, ionization potentials, and heats of formation. Of course, it can be used analytically to identify new compounds and to study reaction rates. In addition to this the technique is extremely frugal of sample material, making it ideal for the study of rare or low-yield compounds.

The low sample requirement makes mass spectrometry especially suited to the study of boron hydride chemistry where yields from reactions are typically low. The first recorded report of a mass spectrum of a boron hydride was reported by Hipple in 1940.¹ No other work was reported until 1948² and 1949.^{2,3} Since then there has been an increasing quantity of information produced in this field; the use of mass spectrometry to determine molecular weights is described in almost every report of a new neutral compound.

General Characteristics of Boron Hydride Mass Spectra

The mass spectra of any boron hydride is extremely distinctive. A hydrocarbon of comparable molecular weight usually has a rather simple spectrum; if it is a saturated molecule, its spectrum has a characteristically low intensity in the high m/e range. In the low m/e range, there are several intense peaks surrounded by relatively weaker neighbors. Conjugated molecules, including aromatics, show the greater strength of their core structure in an even simpler spectrum in which one or two high m/e peaks (often the parent ion is one of them) account for almost the entire intensity. The boron hydride, however, shows a continuous range of multiplets from parent ion to B^+ . The base peak is not the parent ion peak, which is often quite small, but is typically several mass units below it. Each multiplet is pyramidal in shape (Fig. 1), and intensity decreases toward low m/e .

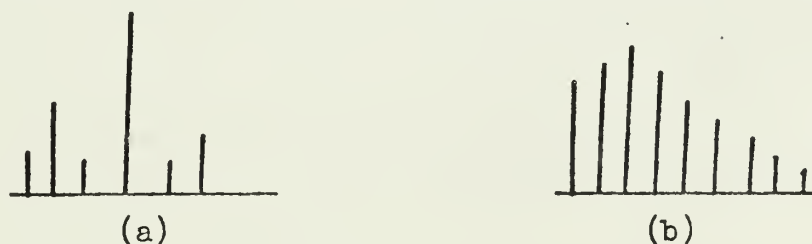


Fig. 1 (a) typical hydrocarbon multiplet
(b) typical boron hydride multiplet

The boron hydride spectrum is explained on the basis of several facts. First of all, from other data (x-ray diffraction, etc.) it is known that the core structure of boron hydrides is a cluster of boron atoms which has many of the properties of aromatic systems. Thus, the high intensity high m/e region is understandable. Part of the basis for the multiplet structure is found in the poly-isotopic nature of naturally occurring boron. Boron occurs naturally in two isotopes ^{11}B and ^{10}B , in an approximately four to one ratio. Exactly 4 to 1 is the ratio most often used, some support for this being the actual $^{11}\text{B}/^{10}\text{B}$ ratio has been found.⁵ (Natural carbon is practically monoisotopic, only 1.11% ^{13}C .) Thus corresponding to an ion species containing several boron atoms there will be more than one mass number and hence more than one peak. This can be treated statistically⁴ as a weighted binomial distribution with each peak's intensity proportional to a term in the expansion of

$$(p + q)^n \quad \text{where}$$

p = the probability of one isotope

$q = (1 - p)$ = probability of other isotope

n = number of boron atoms .

But for a peak corresponding to $^{11}\text{B}_x\text{H}_n^+$ there will also be a contribution to the intensity from $^{10}\text{B}^{11}\text{B}_{x-1}\text{H}_{n+1}^+$ if this latter ion occurs; it may be assumed, however, that the highest m/e peak derives its intensity from only one ionic species. Using this, the statistical isotope distribution corresponding to the same structure can be calculated and subtracted from the intensities at the m/e values indicated. The monoisotopic intensity of the ionic species can be determined by summing the distribution. This process then can be repeated for the next peak, and so on.⁴ Multiplets with B_n to B_1 are seen; the individual multiplet is due to variations in the number of hydrogens attached to the core.

One other feature appears; the base peak is often preceded and sometimes followed by several intense peaks separated by two units with intervening peaks of lower intensity.^{4,6,7} This phenomenon, often seen in hydrocarbons though seldom as pronounced, is caused by H_2 elimination.⁸ A correlation has been seen in the number of hydrogens removed before the base peak and the number of boron atoms which have bridge hydrogens.⁹ But the prime correlation seems to be between the number of H_2 units eliminated and the number of bridge hydrogens in the parent molecule. A study of μ -tetradeuterio-decaborane-14 indicated that most of the H_2 eliminated was eliminated as HD .¹⁰ Apparently one cage hydrogen is eliminated with each bridge hydrogen; this pair represents the closest H-H approach in the parent molecule.

An isotope effect is to be expected in the relative intensities of the different ions; differences are found, but they are not sufficient

to affect the overall appearance of the spectrum. Mono-isotopic stripped spectra of the same compound with different isotopic content are easily recognizable as being of the same compound.¹¹

Applications

I. Structural: The most common use of mass spectrometry in boron chemistry has been in synthetic characterization via confirmation of the expected molecular weight by the spectral cut-off.^{12-18,54} One variation of this technique which gives more information involves the use of isotopes. Comparison of the cut-off values for the spectra of the same compound prepared with ¹⁰B and/or ²H with the spectrum of an isotopically normal sample determines the number of hydrogen and the number of boron atoms present.^{19,20,21}

In addition there have been many instances in which mass spectrometry has been used in an analytical mode to compare new compounds to known ones.²²⁻²⁹

Mass spectrometry has also been used to detect new compounds in mixtures formed in electric discharge,³⁰ pyrolysis,³¹ aging,³² and shock tube³³ experiments.

II. Thermodynamics: The use of mass spectrometry to determine thermodynamic properties of substances through the appearance potential method is well known. In boron hydride chemistry many studies of this type have been done by W. S. Koski and co-workers.^{35-38,46,47} In their work they have used the critical slope method, occasionally with some modification, to determine appearance potentials. The main difficulties encountered are the isotope multiplets and the lack of knowledge of the structures of the ions in question. Usually the appearance potential is determined by monitoring the intensity of one peak as a function of the electron retarding potential; in a polyisotopic case this is impossible due to multiple contributions to the intensity. Two solutions are possible: first, scan a sufficient m/e range to strip the desired peak for each value of the retarding potential; or second, use isotopically pure material. The latter method is more usual, although the other method has been used.

In order to get meaningful information from appearance potentials, the usual equation must be employed.

$$A(R_1) = IP(R_1) + D(R_1-R_2)$$

Since the ions are not of sufficient stability to be isolated in their neutral form, independent studies of ionization potentials are not possible. In most instances the investigators have sought to determine ionization potentials by approximating $D(R_1-R_2)$ from thermochemical bond energies; this approach requires three assumptions—

1. bond structures for the ion and fragment can be determined
2. bond energies are constant from compound to compound
3. localized bonding can describe cage bonding.

However, as more studies are reported, a self-consistent system can be generated.

III. Kinetics and Mechanistics: Kinetic and mechanistic investigations can be divided into four types:

1. Simple: Mass spectrometry can be used to repeatedly determine the concentration of reactants by scanning or to monitor the concentration of one by operating in a stationary mode.³⁹ This method has the advantage over chemical analysis in that the samples taken are too small to affect the conditions.
2. Labeling: Mass spectrometry can be used to determine the rate of an exchange reaction using stable isotopes as tracers. The degree of exchange can be determined using the weighted binomial distribution mentioned above by allowing p and q to be variables. In this method the two reactants need not be isotopically pure but only have different isotopic composition.⁴⁰⁻⁴⁴
3. Metastable Ion: Koski and Fehlner have determined the complete dissociation scheme for tetraborane-10⁴⁵ from B_4H_{10} to B_4^+ . They used the relationship $m^* = m_2^2/m_1$ to determine the reaction leading to the metastable ion, and confirmed this with a comparison of the appearance potentials of m^* and m_1 . They have also done a similar study of pentaborane-9, pentaborane-11, and hexaborane-10; they were, however, not able to deduce so extensive schemes as that for tetraborane-10.⁴⁷
4. Intermediate Detection: Mass spectrometry may be used to search for an intermediate in a reaction, thus confirming the proposed mechanism. Much current use is being made of this method to study pyrolysis reactions of boron hydrides. This procedure is usually done with a specially designed or modified instrument.⁴⁸⁻⁵³

Conclusion

Several avenues for extension exist in this field: 1) application of existing techniques to new compounds such as carboranes and transition metal derivatives, 2) the introduction of new techniques such as high resolution mass spectrometry. With one exception, the results reported so far are not of highest resolution. M. F. Hawthorne recently reported the cut-off value for several transition metal derivatives as high resolution values.⁵⁴ This technique should prove valuable, as the mass difference between ^{10}BH and ^{11}B is 0.011 amu and a difference of 0.005 amu should be resolvable. Thus the polyisotope confusion would not occur in high resolution work.

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BONDING AND REACTIONS OF COORDINATED LIGANDS IN METAL ACETYLACETONATES

J. Thatcher

March 14, 1967

Introduction

Chemists have only recently begun a systematic investigation of the chemical behavior of coordinated ligands.^{1,2,3,4} These studies have improved our understanding of the role of coordinated metal ions in catalysis and biochemical synthesis.

Fernando³ has given the following definition: "When a system consisting of a metal ion, a ligand and one or more metal-ligand complexes undergoes a reaction in which the ligand is transformed into one or more compounds which may or may not be ligands, the reaction can be considered to be a coordinated ligand reaction."

One aspect of coordination chemistry that has been of interest throughout the years is the nature of the metal chelate ring. The type of bonding⁵ present in these ring systems, the influence of the ring systems on the rest of the molecule, and especially the aromaticity⁶ of such rings have been controversial subjects.

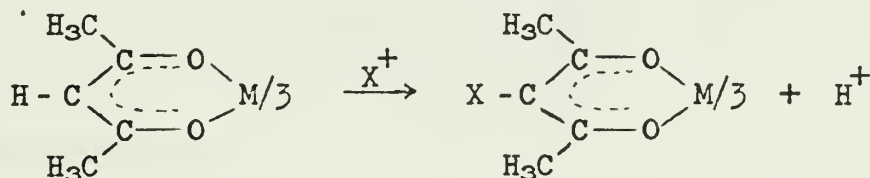
This seminar will be concerned with the reactivity of acetylacetone and some of its derivatives when coordinated to the transition metal ions Cr(III) and Co(III), and some of the physical evidence regarding the electronic structure of these metal chelates.

Complexes

Free acetylacetone exists in two forms, keto and enol. Loss of the enol hydrogen produces the enolate ion which is the chelating species. Chelates of virtually every metal have been reported. Fackler⁷ has recently reviewed metal ketoenolates.

Acetylacetone readily forms tris complexes with Cr(III) and Co(III). These complexes are kinetically stable nonionic complexes and are amenable to treatment in organic solvents where hydrolytic decompositions can be minimized. Techniques such as crystallization, chromatography, IR, UV, and NMR are useful in characterization and purification. These complexes are amirrocentric and can be partly resolved by chromatography on D-lactose hydrate.⁸ The crystal structure of Cr(AA)₃,⁹ is known.

Electrophilic Substitution of Chelate Ring



X = I, Br, Cl, SCN, SAr, SCl, NO₂, CH₃Cl, CH₂N(CH₃)₂, COR, CHO

Most of the work on substitution reactions has been done by Collman and co-workers.¹⁰ Selective reagents must be employed to minimize degradation of the rings. Mono, di, and tri substituted chelates are formed if the concentration of electrophilic reagent is limited. Mixed ligand complexes in which all three rings are substituted by different groups are prepared by stepwise reactions. Substituents can be displaced by other electrophiles.

The metal chelate ring remains intact throughout the course of the reaction. This has been verified by utilization of radioactive tracers¹² and optically active chelates.¹³ Therefore, it is reasonable to assume that the kinetically active species is the metal chelate. It is generally assumed that the attacking species is X^+ and that the probable mechanism is the chelate ring undergoing S_E2 attack by the electrophile, although detailed mechanistic studies have not been carried out.

No attempt will be made to discuss each reaction. Instead a few examples will be taken to illustrate the interesting behavior of these compounds.

Nitration:

Metal acetylacetonates are most successfully nitrated in a solution formed by $Cu(II)(NO_3)_2 \cdot 3H_2O$ in acetic anhydride. $Cr(AA)_3$ can be catalytically reduced to the amine, which behaves as a typical aromatic amine. The amine has been diazotized. The resulting fluoroborate is stable as a dry solid, but it reacts with water to form a phenol-like hydroxy chelate. The stability of this chelate diazonium salt is the best chemical evidence for the aromatic character of the metal acetylacetonate ring system.

Acylation and Formylation

Acylation occurs under carefully controlled Friedel-Crafts conditions. A mixture of boron fluoride etherate and acetic anhydride is effective. Introduction of an acyl group into one ring apparently deactivates the remaining rings. Acetyl groups are cleaved from the ring by several electrophilic reagents. Cleavage of a C-C bond under such mild conditions is unusual. Introduction of formyl groups also deactivate the rings. Aldehyde groups are resistant to classical carbonyl reactions.

Reactivity of the Ring

Electron density at the central carbon atom of the chelate ring is an important factor in electrophilic reactions. The methyl groups in the chelate rings seem to sterically retard reactions, but electronically they enhance the reactivity of the ring and perhaps shield the oxygens.

Disproportionation

Unsymmetrically substituted tris acetylacetonates of $Cr(III)$ and $Co(III)$ disproportionate¹⁴ in solution at elevated temperatures.

Linkage isomerism accompanies intermolecular ligand exchange in formyl and chloro substituted chelates of Cr(III) and Co(III). The linkage isomer represents a type of cobalt complex which previously couldn't be synthesized due to oxidation of the aldehyde group.

NMR Spectra

The proton NMR spectra of the diamagnetic cobalt chelate provides a useful method of structure determination. There are no spin-spin coupling effects and the unsubstituted acetylacetonate exhibits proton signals in the ratio of 1:6 due to the central hydrogens and the equivalent methyl hydrogens. Trisubstitution results in disappearance of the former peak and shifting of the methyl signal to lower field. The chemical shift of the methyl protons in trisubstituted chelates depends on the substituent, the ring, the metal, and the solvent.

Anisotropic Shielding Effects

Unsymmetrically substituted tris acetylacetonates exhibit an unexpected chemical shift.^{4,11} In disubstituted chelates the two methyl groups on each of the two equally substituted rings are not equivalent and give rise to two sharp signals. The methyl groups on the other ring give one sharp signal. Each methyl group on one ring is over the symmetry axis of another ring due to the rigid geometry of the molecule. Chelates in which all three rings are differently substituted exhibit six methyl signals.

Interannular Electronic Effects

The NMR of partially substituted cobalt and rhodium chelates shows that the chemical shift of the signal for the central hydrogen atom in the unsubstituted chelate ring depends on the substituents on the other rings.^{10,11}

Spin Delocalization

Eaton¹⁵ has recently studied the proton NMR spectra of paramagnetic transition metal acetylacetonates and concluded that the proton shifts of the ligands were due to a contact interaction between protons and electron spin delocalized from the metal to the ligand π orbitals. He discussed his results in terms of spin delocalization due to both metal-to-ligand and ligand-to-metal charge transfer processes involving π orbitals of the ligand and "d" orbitals of the metal.

Electronic Spectra

The ultraviolet spectra (excluding d-d transitions) of these chelates are complex. One to four bands or shoulders are found. The principal absorption bands occur at about 256 m μ for cobalt and at 331 m μ for chromium acetylacetonate.

Substituent Effects

Forster¹⁶ has studied the effects of substituents on the chelate rings upon the positions of the bands in the 22,-40,000 cm^{-1} region. These shifts are similar in all the bands and in accord with the predictions of MO theory for π - π^* transitions. By comparing the u.v. spectra of substituted acetylacetonates, the extent of steric inhibition of resonance with the chelate ring is indicated.¹⁰

Other Studies

Dipole Moment

Brook and Frieser¹⁷ measured the electric moments of $\text{>C}-\text{Cl}$ and $\text{>C}-\text{NO}_2$ in partially substituted $\text{Cr}(\text{AA})_3$ and found them intermediate between those for aromatic and aliphatic systems. They concluded that electron withdrawing groups cause more back donation from the metal. No effects transmitted through the metal ion were observed.

IR

Infrared spectra are useful in determining substitution products. The disappearance of a weak C-H in-plane bending vibration at 1190 cm^{-1} provides a measure of ring substitution. The type of substitution product can be determined by the characteristic group-frequencies of the substituents. The IR spectra have been actively investigated.^{21,22} Ag^+ complexes of metal acetylacetonates have been prepared and the IR spectra studied.²³

ESR

Electron spin resonance studies^{18,19,20} indicate that there is some π bonding interaction between the metal ion and the ligands in transition metal acetylacetonates.

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FACTORS INVOLVED IN THE STABILIZATION OF
PENTACOORDINATION IN COMPLEXES OF DIVALENT Ni, Pd AND Pt

D. F. DeCraene

March 21, 1967

Introduction

Only in recent years have five-coordinate complexes of Ni(II), Pd(II) and Pt(II) been considered as extending beyond the category of rarities.^{1,2} However, in the last decade especially, several cases of pentacoordinate complexes of these divalent ions have been prepared and characterized. In light of these examples it is now realized that five-coordinate complexes of these metals, though not as common as the four-coordinate cases, are quite easily obtained under proper conditions. The primary purpose of this seminar is to summarize the available cases of pentacoordination of Ni(II), Pd(II), and Pt(II) so as to indicate the conditions necessary to stabilize this coordination number with these metal ions.

Stabilization Factors

In general, the coordination number of a metal ion in a particular oxidation state is determined by the following interrelated factors:³

- 1) the nature of the ligand.
- 2) the types of bonding employed.
- 3) the steric effects inherent in the resulting aggregate species.

It is reasonable to expect that the first of these factors determines the relative degree of participation of the other two. Once the metal ion has been specified, it necessarily follows that the requirements of the complex-forming ligands will determine the nature of the resultant species.

In the cases of pentacoordination of divalent Ni, Pd, and Pt, the factors for stabilization seem to involve a balancing of the degree of contribution from the following factors:⁴

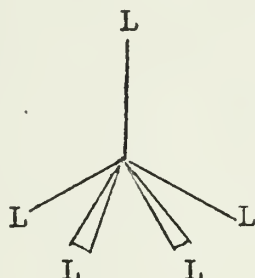
- 1) the relative importance of π -bonding and σ -bonding in the donor atom involved.
- 2) the relative energies of metal atom orbitals which will be incorporated into the coordination scheme.

In general, the evidence may be cited as pointing to an increase in the tendency of a donor atom to promote pentacoordination in the order $N < P < As < Sb$ for Group V. Also, some workers have noted a tendency for a particular ligand to favor pentacoordination to an increased degree in the order $Ni >> Pd > Pt$ for the divalent ions.⁵ Arguments based on a strict

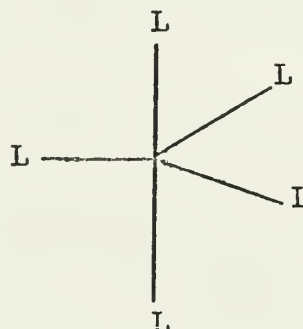
valence bond approach have suggested an explanation which involves the electronegativity of the donor atom, effective nuclear charge of the central metal atom, and the relative energies of separation of the atomic orbitals in the central metal atom. Alternate suggestions involving the π -bonding capabilities of the donor atom have been proposed. While both of these approaches have considerable merit, the observer would be more amenable to an explanation which employs a balance of the π -bonding capabilities of the donor atom, and the ability of metal atom to present an appropriate scheme of available bonding orbitals, as the factors which stabilize penta-coordination. Such an explanation would deal with the recognized facts more realistically and steric factors need be invoked only where weakly π -bonding situations do not allow for use of this factor as an explanation of stabilization. In short an a priori explanation is yet to be presented.

Geometry

The pentacoordinate complexes can be discussed in terms of two idealized geometries.¹ They are the tetragonal pyramid(I), having C_{4v} symmetry, and the trigonal bipyramid(II), having D_{3h} symmetry. Substitution of non-equivalent donor atoms into the coordination sphere changes the point group symmetry, however, it still allows discussion of the complexes in terms of these two spatial arrangements.



(I) - C_{4v}



(II) - D_{3h}

In general the configurations of the individual complexes involve at least a distorted form of either (I) or (II). The degree of distortion relates to the steric demands of the ligand.

Evidence

Confirmed and characterized examples of pentacoordinate complexes of divalent Ni, Pd, and Pt will be presented and discussed in terms of the aforementioned factors. Examples are proposed for monodentate,⁷⁻¹⁴ bidentate,^{4,15,16} tridentate,^{5,17-21} tetradentate,^{18,19,22-30} and even pentadentate³¹⁻³³ ligands.

SUMMARY

It is generally observed that pentacoordination of these metal ions involves ligands which possess π -bonding characteristics or are bulky

multidentate molecules. An attempt to establish a trend in stabilization of pentacoordination as a function of π -bonding has been made. On the basis of these observations, it is quite probable that the stabilization of the pentacoordinate species involves a balance of two factors: 1) the π -bonding ability of the ligand donor atoms to stabilize the increase in coordination number and 2) the energetics of the change in coordination number with respect to the central atom's available orbitals. However, it is apparent that there is real need for more precise knowledge of structures. Such knowledge would enhance the reliability of discussions of bonding in the pentacoordinate complexes of these metal ions.

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CYCLIC PHOSPHINES

Brian Faught

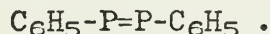
April 4, 1967

Introduction

This seminar deals with the preparation, properties, and some of the reactions of a series of compounds known as the cyclic phosphines. It was only in 1956 that these compounds were recognized as being cyclic, and since that time, a considerable amount of interest has been generated by the workers in this field. There is a chemistry of arsenic which parallels that of the cyclic phosphines. These compounds are prepared in a similar fashion and undergo analogous reactions.

Preparation and Properties

In 1877, Michaelis and Köhler¹ treated phenylphosphine with phenyl-dichlorophosphine and obtained a yellow substance melting at 150° to which was ascribed the structural formulation



This compound was called "phosphobenzene" because it was thought to be analogous to the azobenzene compound. In 1952, Erlenmeyer and his coworkers² reported the preparation of a compound melting at 193° from the same starting materials. Analysis and molecular-weight determinations seemed to indicate the same structure proposed by Michaelis. Reesor and Wright³ confirmed both of these reports and found a third compound melting at 255°. These materials have subsequently been labelled as follows:

<u>Compound</u>	<u>Melting Point</u>
phosphobenzene A	150°
phosphobenzene B	198°
phosphobenzene C	255°

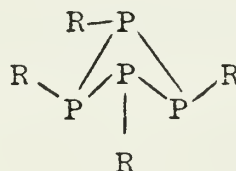
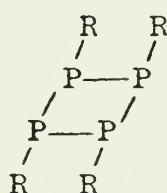
Since that time, many different cyclic phosphine systems have been synthesized. There are listed in review works by Cowley and Pinnell.^{4,4a} Some of the more generally used preparative procedures are described by the equations:

- (1) $n \text{ RFX}_2 + 2n \text{ M} \longrightarrow (\text{RP})_n + 2n \text{ MX}$
- (2) $n \text{ RPH}_2 + n \text{ RPhCl}_2 \longrightarrow 2 (\text{RP})_n + 2n \text{ HCl}$
- (3) $n \text{ RPH}_2 + n \text{ R}_2'\text{Hg} \longrightarrow (\text{RP})_n + n \text{ Hg} + n \text{ R}'\text{H}$
- (4) $2 \text{ RMgBr} + \text{P}_4 \longrightarrow [\text{R}_2\text{P}_4(\text{MgBr})_2]_2 \xrightarrow{2 \text{ FBr}} (\text{RP})_4 + 2 \text{ MgBr}$

Of all the reported compounds, the phosphobenzenes, $(C_6H_5P)_n$ and the trifluoromethylcyclophosphines, $(CF_3P)_{4,5}$ seem to be the most interesting. Cyclopolyphosphines with rings containing three, four, five, and six phosphorus atoms have been reported.

There have been several reports in the literature recently of the detection of the three-membered phosphorus ring system.^{5,6,7} Baudler⁵ reports the separation of P_3H_3 by gas chromatography and its identification by mass spectrograph. Later, he reports⁶ the three-membered phenylcyclophosphine compound, $(C_6H_5P)_3$. Perhaps the most positive identification of a three-membered ring is by Issleib and Fluck,⁷ who prepared a compound $K_2(PC_6H_5)_3$ from $(C_6H_5P)_n$ and potassium metal. It is a crystalline solid which gives a ^{31}P NMR spectrum with a single peak, indicating equivalence of phosphorus atoms, and thus a cyclic system.

The four-membered ring system has been well characterized for the alkylcyclophosphines. In a study of compounds known up to 1960, Issleib and Mitscherling⁸ listed the following order of oxidative stability: $(C_2H_5P)_4 > (cyclo-C_6H_{11}P)_4 > (CF_3P)_4 > (C_6H_5P)_n$. It is interesting to note that this order is approximately the reverse of that of relative electron withdrawal of substituent groups, thus leading support to the theory that delocalization within the ring induces stability. The crystal structure of $(CF_3P)_4$ was reported by Donohue,⁹ and the P_4 ring was shown to possess D_{2d} symmetry. Vibrational analysis¹⁰ of other alkylcyclophosphines, assuming D_{2d} symmetry, indicated that the symmetric and asymmetric P_4 ring stretching frequency is little affected by different alkyl groups. Characterization of the phenylcyclophosphines has not been an easy task, possibly because they are the least stable of the cyclic phosphines.⁸ Numerous molecular-weight studies by Kuchen and Buchwald¹¹ and Henderson et al.¹² indicate that the A form of phosphobenzene in solution is a four-membered ring, as is also the B form.^{3,12} Henderson and his coworkers conclude that A and B are stereoconformers in solution.



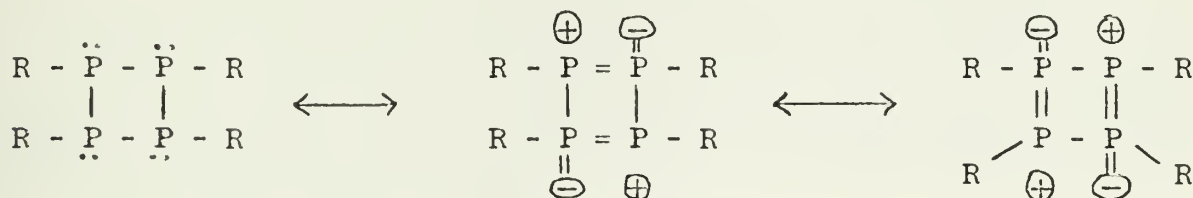
Raman studies have also been reported.¹³ The crystal structures on the A and B forms have been determined,¹⁴⁻¹⁸ and these indicate a five-membered ring for A and a six-membered ring for B in the solid state.

Now, it is generally accepted that in the solid state these compounds have five- and six-membered rings, whereas in solution, they have four-membered ring structures. Several¹⁹⁻²¹ feel that there is an easy conversion from one ring size to another, particularly among the less stable species. Among European workers the concept of phosphorus diradicals $RP\cdot$ seems to be popular in explaining this phenomenon. Recently, there has been some evidence for the presence of the five-membered ring structure in solution.⁶

Theoretical Treatment of the Phosphorus Ring:

When Burg and Mahler first reported the $(CF_3P)_{4,5}$ compounds²⁴ they suggested that P-P sigma bonding was supplemented by π -type interaction

involving delocalization of the lone pair on the phosphorus atom. Recorded ultra-violet spectra of the compounds, $(\text{CF}_3\text{P})_{4,5}$ ²³ and other alkylcyclophosphines¹² seem to indicate that this is true. The following resonance structures have been proposed:

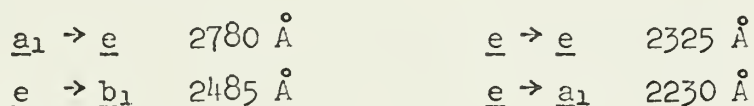


It was found, in general, that in the vapor state the ultra-violet spectra of compounds containing four-membered rings have three absorption peaks, whereas those of compounds containing five-membered rings exhibit only one. A free-electron molecular-orbital (FEMO) approach was applied by Mahler and Burg to the species $(\text{CF}_3\text{P})_{4,5}$. The energy is given by the expression,

$$E_n = \frac{n^2 h^2}{8m^2 m R^2}$$

and the positions of the major peak in each spectrum were calculated and found to be in reasonable agreement with the observed. For the four-membered ring species the values are 2600 Å, calculated and 2590 Å, observed; for the five-membered, 2300 Å, calculated and 2400 Å, observed. Diamagnetism of the four-membered ring, as well as the appearance of more than one absorption peak, was attributed to the non-planarity of the ring.

Cowley and White²⁵ have described an Extended Hückel Molecular Orbital approach to the problem. The need for the 3d orbitals to account for the observed spectra and lack of cross-ring binding were established. A spectrum which agrees quite well with the observed was calculated. Calculated transitions should occur as follows:



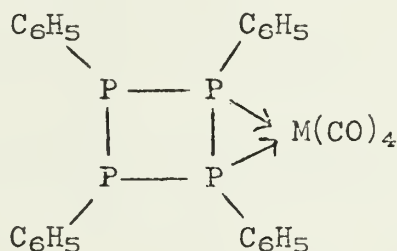
Observed transitions occur at 2590 Å, 2390 Å, and 2210 Å. Since the peak at 2530 Å is quite broad, it may contain both peaks calculated to be at 2485 Å and 2780 Å.

Reactions

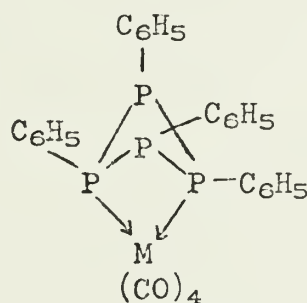
A. Metal Complex Formation

There have been several papers published dealing with complex formation, but the results obtained vary, and seem to be quite dependent on reaction conditions. Burg and Mahler²⁶ have submitted the only report on the tri-fluoromethylcyclophosphines. They describe a compound of composition $[\text{Ni}_{1.77}(\text{CO})_{4.45}(\text{CF}_3\text{P})_4]_x$ obtained from reaction of $\text{Ni}(\text{CO})_4$ and $(\text{CF}_3\text{P})_4$. They suggest that the P_4 ring may be bridging between Ni atoms to give a polymeric structure.

Reactions of metal carbonyls with phenylcyclophosphines have been studied.²⁷⁻³⁰ Ang²⁷ and coworkers report that reactions of $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_5$ with phenylcyclophosphine result respectively in compounds of formulations $(\text{C}_6\text{H}_5\text{P})_4\text{Ni}(\text{CO})_3$ and $(\text{C}_6\text{H}_5\text{P})_4[\text{Fe}(\text{CO})_4]_2$. If tungsten and molybdenum hexacarbonyls are used, "ring expansion" is said to occur with isolation of the compounds: $(\text{C}_6\text{H}_5\text{P})_5\text{W}(\text{CO})_5$ and $(\text{C}_6\text{H}_5\text{P})_5\text{Mo}(\text{CO})_5$. Fowles and Jenkins²⁸ found that if molybdenum, tungsten, and chromium hexacarbonyls are heated with phenylcyclophosphine in a sealed tube at 140°C , complexes which are formulated as $\text{M}(\text{CO})_4(\text{C}_6\text{H}_5\text{P})_4$ are obtained. These compounds are monomeric in benzene solution and appear to be simple cis-substituted carbonyls of the structural type:

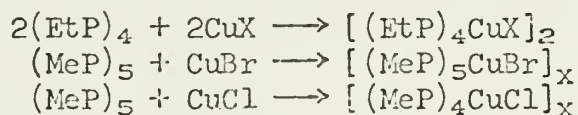


Stone et al.²⁹ indicate that since the four-membered ring is puckered it would probably be more nearly correct to assume the structural formulation:



Cowley and Pinnell³⁰ isolated a compound, $(\text{C}_6\text{H}_5\text{P})_5\text{Ni}(\text{CO})_3$, from the reaction of $\text{Ni}(\text{CO})_4$ with phenylcyclophosphine.

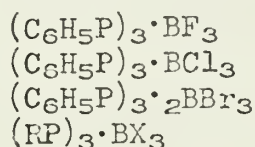
Reactions have also been reported for metal halides.^{29,31} Hicks and Dean describe the preparation of $(\text{RP})_4\text{CuX}$ and $(\text{RP})_4(\text{CuX})_2$, where R is alkyl and X halogen. Stone and coworkers report the reactions described by the equations,



X-ray investigations of some of these complexes are in progress.

B. Boron Halide Complexes

These adducts have been reported by several workers.^{11,23,32} Cowley and Pinnell have recently obtained these following complexes:

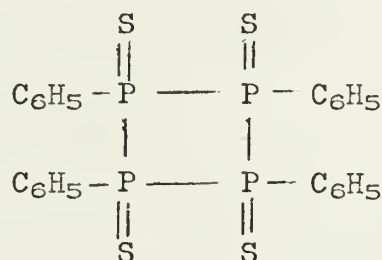


where R = Et, n-propyl; n-butyl and X = F, Cl, Br.

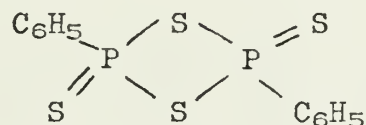
From their infrared spectra the ring structures appear to be intact, but there is no indication of how large the rings are.

C. Reactions with Group VI A Elements

Kuchen and Buchwald¹¹ reported that the reaction of oxygen with phenylcyclophosphine results in the formation of a mixture of polymeric anhydrides of phenylphosphoric acid. Reaction with elemental sulfur in a ratio of one phenylcyclophosphine molecule to four sulfur atoms yielded a compound $(C_6H_5PS)_4$, which has been assigned the structure,^{11,33}



on the basis of infrared spectra and molecular weight data. If sulfur is heated with phenylcyclophosphines in a mole ratio of 8:1, a polymeric substance $(C_6H_5PS_2)_n$, is obtained. Maier³³ has assigned the structural formulation,



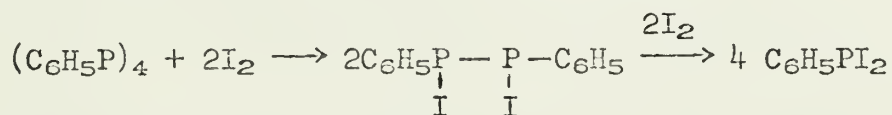
on the basis of infrared spectra and preliminary X-ray data.

Recently, Burg³⁴ has found that a 1:1 ratio of S to $(CF_3P)_4$ leads to a five-membered heterocyclic ring compound.

Tetraphenylcyclotetraphosphine tetraselenide has also been prepared by the reaction of $(C_6H_5P)_4$ with elemental selenium.³⁵ The analogous reactions with tellurium did not yield a product.

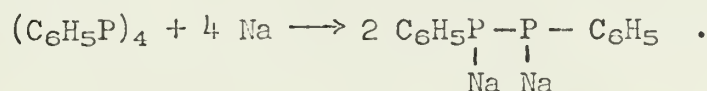
D. Reactions with Halogens

The cyclophosphines undergo ring cleavage with chlorine, bromine, and iodine.^{3,11,23} The reaction appears to take place stepwise, as has been shown for the iodination of phenylcyclophosphine.



E. Reactions with Alkali Metals

Phenylcyclophosphine is only partially cleaved at room temperature by sodium in diglyme:



If sodium or lithium is allowed to react with phenylcyclophosphine in tetrahydrofuran^{11,36}, total cleavage takes place. Cleavage of the ethyl and cyclohexyl derivatives in tetrahydrofuran by potassium metal is only partial.

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RECENT STUDIES OF PEROXYCHROMIUM COMPLEXES

E. P. Hertzenberg

April 11, 1967

Introduction

Chromium compounds containing peroxy groups have been known for over 100 years and a large number of these complexes were prepared during the early 1900's.¹ These compounds, most of which are unstable, are of interest since the chromium seems to exhibit two unusual oxidation states, Cr(IV) and Cr(V), as well as the more familiar Cr(VI).

Within the past ten years the use of X-ray and other spectral techniques has greatly increased the chemist's knowledge of these compounds, and they are now most easily classified according to the chromium oxidation number.

Compounds of Cr(V): $M_3Cr(O_2)_4$

Compounds of this general formula are easily prepared by the action of H_2O_2 on alkaline chromate solutions. Wilson² performed the first X-ray structural analysis of a peroxychromate and found that the CrO_8^{-3} ion has D_{2d} symmetry, with a distorted dodecahedral arrangement of oxygen atoms around the central chromium atom. The chromium forms an approximately isosceles triangle with each of the peroxide groups. Stomberg^{3,4} confirmed this structure, concluded that one oxygen of the peroxide group is slightly closer to the chromium atom than the other, and that the O-O distance is slightly shorter than the O-O distance in solid H_2O_2 and BaO_2 .

Ligand field calculations based on the dodecahedral symmetry were done by Ibers.^{5,6} A Δ value of $35,000\text{ cm}^{-1}$ was found; from ESR studies the presence of appreciable covalency in the chromium-peroxide bonding was noted. A similar ESR study by McGarvey⁷ confirmed this conclusion.

Compounds of Cr(VI): a) $BCrO(O_2)_2$

The parent compound, CrO_5 , is called "blue perchromic acid" and may be prepared by the reaction of H_2O_2 with acidic dichromate solutions. CrO_5 is a Lewis acid and has been observed only as an adduct with Lewis bases such as ethers, esters, amines, alcohols, ketones, and nitriles. Aqueous solutions of perchromic acid are unstable. Unstable solid adducts are formed with heterocyclic nitrogen bases such as pyridine, dipyridyl, phenanthroline, and quino-line.

In 1957, studies using Job's method of continuous variations,^{8,9} careful elemental analysis, and infrared spectra⁹ confirmed that the formula of perchromic acid is CrO_5 and not $HCrO_5$ as had been previously believed.

An X-ray structure determination^{10,11} of the $PyCrO_5$ complex shows a distorted pentagonal pyramidal arrangement with the oxo group at the apex. The pyridine plane is tilted 45° from the basal plane, which contains the pyridine nitrogen atom.

Determination of the crystal structure of the phen CrO_5 complex¹² indicated a distorted pentagonal bipyramidal arrangement with the oxo group and one of the phenanthroline nitrogens at the apices.

b) $R[XCrO(O_2)_2]$

The violet salts, where $X = OH^-$, may be prepared 1) by the addition of aqueous KOH or NH_3 to a solution of CrO_5 or 2) by the action of H_2O_2 on neutral chromate solutions. The addition of acid forms blue CrO_5 again. Until 1962 the salts were generally believed to contain an ion of the formula $Cr_2O_{12}^{2-}$.¹³ However, with the use of conductivity, careful elemental analysis, and infrared spectra, Griffith¹⁴ finally confirmed the formula, $M[CrO(O_2)_2OH]$, for this series of salts and that an acid-base equilibrium exists with aqueous blue perchromic acid, $[CrO(O_2)_2OH_2]$.

Compounds where $X = Cl^-$ have been prepared recently.^{15,16} This suggests the possibility that other anionic compounds may be prepared, also.

Compounds of Cr(IV): $B_3Cr(O_2)_2$

These are the most stable of the peroxychromates. The triammine complex, $(NH_3)_3CrO_4$, has a distorted pentagonal bipyramidal structure^{17,18} with C_{2v} symmetry, since two of the three ammine nitrogens are in apical positions. The first structural determination¹⁷ indicated an extremely short O-O bond distance and led to the conclusion that the O-O group is a superoxide. This was refuted by Stomberg¹⁸ and was criticized by many other workers.

The ionic complex, $K_3[CrO_4(CN)_3]$, was found¹⁹ to have a structure similar to that of the triammine complex. The CN^- groups are bonded through the C atom.

The structure of the complex, $[en(H_2O)CrO_4] \cdot H_2O$,²⁰ has also been determined.

The diethylenetriamine complex,²¹ $[dienCrO_4] \cdot H_2O$, has been prepared. Recently, the use of $[dienCrO_4] \cdot H_2O$ and $[en(H_2O)CrO_4] \cdot H_2O$ as intermediates in the synthesis of some new dien and en complexes has been reported.²² More recently, B_3CrO_4 complexes containing propylenediamine and butylenediamine have been prepared.²³

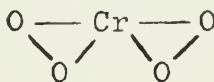
Bonding in the Peroxychromium Complexes

A ligand field representation of the metal-peroxide bonding has already been discussed for K_3CrO_8 . In terms of the valence bond theory the seven-coordinate complexes are considered to be d^3sp^3 hybrids while the eight-coordinate complexes are d^4sp^3 hybrids.

Griffith²⁴ proposed a "bent bond" scheme to explain the observed shortening of the Cr-O and O-O bond distances.

Tuck^{25,26} considered the peroxide group to be a monodentate ligand and the Cr(V) and Cr(VI) compounds to have distorted tetrahedral structures. The peroxide group is a π -donor to the unfilled "d" orbitals of the chromium atom. No back-bonding, such as occurs in Pt-olefin complexes, is possible since the "d" orbitals are unfilled and the π^* orbitals of the peroxide are filled.

The π -donor scheme was used²⁷ to explain the occurrence of peroxide groups in pairs in the planar arrangement represented below.



Conclusion

Now that a number of structural determinations have been made, attention has been shifted to the synthesis of new peroxochromium compounds and to the kinetics of formation^{28,29,30} and decomposition of those already prepared.

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RECENT APPLICATIONS OF ELECTROCHEMICAL
TECHNIQUES TO INORGANIC CHEMISTRY

Albert McDaniel

April 18, 1967

Introduction

In the past twenty years electrochemical theory and instrumentation have developed rapidly. An advance in the instrumentation gave impetus to the theory which demanded even more advancement in the instrumentation. The process is continuing and has reached the point where a few types of electrochemical measurements can be made in the microsecond region.

The application by inorganic chemists of electrochemical techniques, with the exception of polarography, has been very slow. The purpose of this seminar is to present some aspects of the theory, instrumentation and application of controlled-potential electrolysis, cyclic voltammetry and chronopotentiometry.

For initial study of the subject, the books by Delahay¹ and Lingane² are recommended.

Controlled-Potential Electrolysis

The method of controlled potential electrolysis is a valuable synthetic tool for it allows one to perform one and only one reaction at the electrode. If the potential of the electrode—not the potential applied to the cell as a whole—is not controlled, side reactions will occur. If a side reaction does occur at the electrode, and if it involves only solvent or supporting electrolyte, possibly no undesirable transformations will be produced in the product or reactant. Unfortunately with uncontrolled potential, the product or reactant will often react to give another species.

The instrumentation^{3,4} may be simple or sophisticated. The basic requirements are (1) a variable voltage DC power supply, (2) a reference electrode and potential indicator, (3) a feedback network, and (4) a cell. One completely automatic instrument can be built for about \$135.³

It has been stated that the proper choice of potential is vital. The most useful way to determine the potential is by standard DC polarography of the compound if the reaction is a reduction; if the reaction is an oxidation, voltammetric curves at a Pt electrode may be used.

The application of controlled potential electrolysis to synthetic work is obvious. It has definite advantages and disadvantages compared to chemical oxidizing and reducing agents. Controlled potential electrolysis allows selective oxidation or reduction which often cannot be obtained chemically. If the current during the electrolysis is recorded as a function of time, then the electron change involved in the reaction can be determined. The chief disadvantage of controlled-potential is that it is usually much slower than chemical methods: for example, to produce one mole of product which requires two Faraday's requires about 500 hours when using a current of 0.1 amp.

DC Polarography

In order to make comparisons between cyclic voltammetry and polarography, a brief review of polarography is given here. Polarography by definition is the means of determining current-potential, voltammetric, curves using the dropping mercury electrode (DME).

In standard direct current (DC) polarography a voltage varying linearly with time is applied to a DME. The rate of change of voltage in DC polarography is about 10^{-3} volts/sec.

A current-time curve is obtained which is easily converted to a current-potential curve. The most important parts of the curves are the half-wave potential, $E_{1/2}$, and the limiting diffusion current, i_d . The half-wave potential is defined to be the potential at which $c_{ox} = c_{red}$ where c is concentration, ox is the oxidized species and red is the reduced species.

Cyclic Voltammetry

Cyclic voltammetry is a method whereby a potential which varies linearly with time is applied to an electrode. Unlike DC polarography, the voltage first increases then decreases, i.e. the voltage-time curve has the shape of an isosceles triangle. Thus the species in solution are first reduced and then oxidized or vice-versa.

The instrumentation⁵⁻⁷ uses operational amplifiers in standard circuits and is usually assembled according to the experimental precision desired. The basic requirements are (1) a reference electrode and potentiostat to control the potential of the working electrode, (2) a triangular wave generator, (3) a current measuring resistor and output indicator (either a recorder or oscilloscope) and (4) a cell.

The theory is not discussed here, but the reader is referred to the literature.⁸⁻¹¹ Quantitative usage of the current-potential curves obtained demands a computer. Some qualitative aspects of the system can be ascertained merely by looking at the current-potential curves as produced by the oscilloscope or recorder. Other qualitative or semi-quantitative attributes can be shown by a few simple graphs.

By merely viewing the current-potential curves one can readily determine the number and type (reversible or irreversible) of charge transfers. If the potential at which the cathodic sweep is changed to anodic is not less than $35/n$ millivolts past the cathodic peak, where n is the number of electrons involved in the charge transfer and the separation between the cathodic and anodic peaks is $60/n$ millivolts, then the charge transfer is reversible; if the separation is greater than $60/n$ millivolts, then the charge transfer is irreversible.¹²⁻¹⁶

Cyclic voltammetry is also useful in the study of kinetics of a chemical reaction preceding or following a charge transfer or coupled between two charge transfers. Again the reversibility of the chemical step may be easily ascertained by study of the current-potential curves and other simple plots such as i_a/i_c vs. v where i_a is the anodic peak current, i_c is the cathodic peak current and v the rate of voltage scan. For example, if i_a/i_c vs. v is a straight line of slope 0 and intercept 1.0 then the reaction is either a reversible charge transfer or a reversible charge transfer followed by a catalytic chemical reaction.

If the diffusion coefficient of the species and the area of the electrode are known, then the rate constant for a chemical transformation can be calculated. Instrumentally the rate of voltage scan may be varied by a factor of 10^6 ; thus, many strictly chemical—as opposed to charge transfer—reactions may be investigated.

Chronopotentiometry

Chronopotentiometry is the last technique to be discussed; the term stands for time measurement of potential. Thus the current is now held constant and the potential of the working electrode is measured. The instrumentation^{17,18} can be quite simple; the basic requirements are: (1) a constant current power supply, (2) a recorder or oscilloscope, and (3) a cell.

Chronopotentiometry and closely related methods are also useful for studying electrochemical processes¹⁹⁻²⁴ and can be used to study the same types of mechanisms as cyclic voltammetry. The mathematics, and consequently the theory,²⁵⁻³⁰ necessary to solve the differential equations are simpler, but unfortunately the data obtained experimentally are not sufficient to differentiate between mechanisms which have two consecutive steps in common; i.e., an electron transfer—chemical reaction—electron transfer can often not be differentiated from an electron transfer and chemical reaction mechanism.

The applications to inorganic systems are more limited than cyclic voltammetry for the reason listed. Delahay, however, has used chronopotentiometry to determine that Cu(en)_3^{2+} is reduced directly without previous dissociation.³¹

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COORDINATION NUMBERS IN CHELATE COMPLEXES OF THE LANTHANIDE IONS

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Introduction

The outstanding features of the tripositive lanthanide ions are (a) their tendency to form predominantly electrostatic bonds and (b) their large ionic radii, with a steady decrease in size across the series (La 1.016 Å to Lu 0.848 Å). As a consequence of these two features, the ability of these ions to form stable complexes is rather limited, and indeed they form few stable complexes with other than polydentate ligands. On the basis of ionic radii, using a hard-sphere model, one would predict coordination numbers for the lanthanide ions decreasing from nine for La(III) to seven for Lu(III) with an anion such as oxide. Such coordination numbers are indeed observed in many of the crystalline oxides, salts, and hydrated salts of the lanthanides.¹ In dilute aqueous solution, the lanthanide ions appear to have a first coordination sphere containing eight to nine water molecules, with a tendency toward smaller hydration numbers for the heavier ions.^{2,3,4}

A large number of polydentate ligands have been shown to form stable complexes with the lanthanides.^{5,6,35} The stoichiometry of many of these complexes is such that a coordination number of six for the lanthanide ion was readily assumed. However, recent work has shown that coordination numbers larger than six are the rule rather than the exception in lanthanide complexes. This seminar presents evidence for higher coordination numbers in some representative chelate complexes of the tripositive lanthanide ions and discusses the stereochemistry.

The simplest and most basic evidence for coordination number N is provided by compositions of complexes in which N potential donor groups are present. Methods such as those involving thermal analysis, conductivity, molecular weight, and infrared spectra must then be used to determine whether all the groups present are indeed coordinated to the metal ion. Application of these methods to lanthanide complexes does not differ from their application to other electrostatically bonded complexes. In contrast, the use of electronic spectra to investigate the arrangement of the coordinating groups around the central metal ion has some unique features in complexes of the lanthanide ions.

The visible spectra of the lanthanide ions, which result from $f-f$ transitions, differ profoundly from those of the d -transition metal ions. Because the $4f$ orbitals lie largely within the $5s$ and $5p$ orbitals, the effects of crystal fields are generally much smaller than spin-orbit coupling. Therefore the effect of crystal fields is to remove some or all of the degeneracy of the $2J + 1$ -fold degenerate J states of the free ion. For ions with an even number of electrons, i.e., with integral

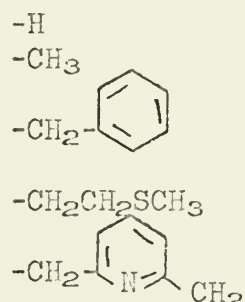
values of J , four general symmetry classes can be distinguished as a result of this splitting: cubic, hexagonal, tetragonal, and all lower symmetries.³⁴ For ions with an odd number of electrons, only two general symmetry classes can be distinguished: cubic and all lower symmetries. For any particular value of J , all of the point symmetries within one of these classes cause the same degree of splitting. Further distinctions can be made, however, by the use of selection rules and by the polarization of the bands.

Crystal structures, which provide the ultimate determination of coordination number and symmetry for crystalline solids, have been determined by x-ray methods for only a few chelate complexes of the lanthanide ions. This situation is at least partly due to the rather complex geometry of many lanthanide complexes.

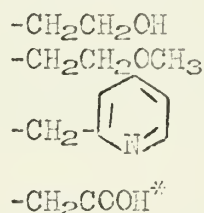
Aminepolycarboxylic Acid Complexes

This group of ligands provided some of the earliest evidence for high coordination numbers in lanthanide complexes. Chemical evidence for coordination numbers of eight or more was provided by the work of Thompson, who measured stability constants for the lanthanide complexes of some N-substituted derivatives of iminodiacetic acid.⁷⁻¹¹ These ligands have the form $RN(CH_2COOH)_2$ with the following N-substituents:

Non-bonding



Bonding



* Stability constants for $R = -CH_2COOH$ were measured by Anderegg.¹²

The bis complexes of the ligands with bonding N-substituents were found to be significantly more stable than those of the ligands with non-bonding N-substituents. This indicates that in the bis complexes both ligands are tetradentate.

Crystallization of EDTA complexes of the lanthanide ions from aqueous solution produces hydrated crystals which cannot be dehydrated without decomposition of the complex, indicating probable coordination of one or more water molecules to the lanthanide ion.^{13,14} The use of infrared spectra to determine whether all of the carboxyl groups of EDTA are bonded to the metal ion gave rather inconclusive results. The spectra of $HLn(EDTA) \cdot xH_2O$ show the presence of more than one type of carboxyl group, whereas those of $NaLn(EDTA) \cdot xH_2O$ salts show only one type of carboxyl group.^{13,14} A determination of the crystal structure of $HLa(EDTA) \cdot 7H_2O$ showed that all six of the coordinating sites of the EDTA molecule, as well as four water

molecules are bonded to the metal ion.¹⁵ The two nitrogen atoms, four oxygen atoms, and one water molecule are positioned at seven of the eight vertices of a quasi-D_{2d} dodecahedron. A substantial out-of-center displacement of the La(III) ion (away from the nitrogen atoms) allows coordination of the additional water molecules. The crystal structures of KLa(EDTA)·8H₂O and NaTb(EDTA)·8H₂O differ from this only in that one less water molecule is coordinated to the metal ion in these salts.^{16,17} The stereochemistry of these complexes is apparently determined by steric requirements of the ligand.

Beta-diketone Complexes

In contrast to those of the corresponding transition metal ions, the tris(acetylacetonate) complexes of the lanthanide ions can be prepared only as the hydrates.¹⁸ A molecule of trihydrate readily loses two water molecules, but attempts to remove the last water molecule result in decomposition. In crystals of the dihydrate both water molecules are firmly held and appear to be coordinated.¹⁹ An x-ray determination of the crystal structure of Y(acac)₃·3H₂O shows that the yttrium ion is 8-coordinate, being bonded to two of the three water molecules.²⁰ The geometry of the coordination sphere is that of a distorted square antiprism.

Generally the anhydrous complexes of the form Ln(RCOCHCOR')₃ are amorphous and have broad, complex spectral bands, whereas the hydrated complexes are crystalline and have sharp, less complex spectra.²¹ Exceptional are those complexes in which R and R' are large, bulky groups. In these complexes steric factors apparently stabilize the 6-coordinate forms.^{21,22,23} With Lewis bases the tris chelates form adducts, the spectra and other properties of which indicate that the base is bonded to the lanthanide ion.^{24,25,26}

The stereochemistry of 8-coordination with four bidentate ligands was discussed by Hoard and Silverton.²⁷ The most favorable geometries are the dodecahedron with D_{2d} symmetry and the square antiprism, which has D_{4d} symmetry. These symmetries may be lowered to S₄, D₂, C₂, or C₁ for the dodecahedron and D₄, D₂, or C₂ for the antiprism, depending on which edges are spanned by the bidentate ligands.

Because of their potential applications in lasers, the tetrakis beta-diketone complexes of europium(III) have been extensively studied. A number of studies have made use of the fluorescence emission spectra of these complexes to determine the symmetry of the complexes.^{21,28,29,30,31} Splitting of the ⁵D₀ → ⁷F₂ band in these complexes generally yields either two or three bands, depending upon the nature of R and R' in the ligands, RCOCHCOR'. The resulting symmetries are D_{2d} for the two-band species and D₂ or S₄ for the three-band species. The splitting of other bands in the spectra add little additional information, but generally support these conclusions. Polarized absorption and fluorescence spectra for the diphenyl derivative indicate that S₄ is the correct symmetry.³² The x-ray crystal structure of the salt CsY(HFA)₄ (HFA is hexafluoroacetylacetonate) shows that the eight oxygen atoms are arranged in a dodecahedron about the oxygen atom and that the overall symmetry of the complex is D₂.³³ The crystal structure of NH₄Pr(TTA)₄·H₂O (TTA is thenoyltrifluoroacetate) is very similar.³³

In solution, the tetrakis chelates are partially dissociated to tris species, the spectra of which show that they are probably strongly solvated.²¹ The tetrakis complexes also form adducts in which the metal ions are apparently 9-coordinate.^{21,30} This alteration can be accomplished by a slight distortion of the dodecahedral arrangement toward the antiprismatic, which provides larger holes for coordination of the Lewis base-type donor molecules.

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ELECTRON SPIN RESONANCE STUDIES OF SIMPLE FLUORINE CONTAINING RADICALS

Gary McPherson

May 2, 1967

Introduction

A radical can be thought of as a molecular fragment containing an unpaired electron. Thus, radicals are suitable for electron spin resonance studies. It is the purpose of this seminar to illustrate the use of this technique in elucidating the nature of radicals. Simple fluorine containing radicals have been chosen here as examples because the work in this field is rather recent and it demonstrates a variety of experimental methods. Naturally occurring fluorine consists of only one isotope, F^{19} , with a nuclear spin of one half. This is ideal for electron spin resonance work.

Elementary Electron Spin Resonance Theory for Radicals

In electron spin resonance spectroscopy one observes transitions between electron spin states which have been split in an external magnetic field. The transition energy generally occurs in the microwave region of the electromagnetic spectrum for moderately large fields (1,000-10,000 gauss). Since these transitions are between spin states, a Hamiltonian which operates only on the spin wave function of the unpaired electron can be used to describe the energy levels involved. This spin Hamiltonian can be simply minded thought of as a collection of terms that describe all the factors that influence these energy levels. For a simple radical containing an atom with a nuclear moment and a single unpaired electron, the spin Hamiltonian can be written as:

$$H_{\text{spin}} = g\beta H_0 S_z + g_n \beta_n H_0 I_z + aI \cdot S + a'I \cdot S$$

The first term in this Hamiltonian is the electronic Zeeman term. This term arises from the interaction of the magnetic moment of the unpaired electron with the applied magnetic field. The quantities in this term are defined as:

- g = electronic spectroscopic splitting factor
- β = Bohr magneton
- H_0 = magnetic field (applied along the z axis)
- S_z = spin quantum number along the z axis

This interaction results in a splitting of the two electronic spin states and leads to the fundamental ESR transition.

The second term in this Hamiltonian is the nuclear Zeeman term. This results from the splitting of the nuclear spin states by the applied field. The quantities involved are analogous to those in the electronic term. The splittings here give rise to the fundamental NMR transition. They are much smaller than the electronic splittings.

The last two terms are called hyperfine terms. They are due to the interaction of the nuclear magnetic moment with the electronic magnetic moment. The first of these terms is the isotropic contact term. "a" is defined as:

$$a = -g\beta g_n \beta_n |\psi_0|^2$$

where: $|\psi_0|^2$ is equal to the unpaired electron density at the nucleus. This contact effect is independent of the direction of the applied field, but is dependent on the electron density at the nucleus. Only s type orbitals have a non-zero density at the nucleus. Thus, a qualitative estimation of the s character of the orbital containing the unpaired electron can be obtained from the observed isotropic hyperfine splitting.

The second hyperfine term is the dipolar term. "a'" is defined as:

$$a' = g\beta g_n \beta_n \left\langle \frac{3 \cos^2 \alpha - 1}{r^3} \right\rangle_{\text{avg}} (3 \cos^2 \theta - 1)$$

where: r is equal to the distance from the nucleus to the electron.

α is the angle between r and the molecular axis.

θ is the angle between the applied field and the molecular axis.

This dipolar interaction is dependent upon the angular orientation of the radical with respect to the magnetic field. Unlike the contact effect, only non s orbitals contribute to this type of interaction.

How this anisotropic interaction affects an ESR spectrum varies with the experimental conditions. A radical oriented in a single crystal will exhibit a spectrum which is dependent on the orientation of the crystal in the field. A randomly orientated radical will show a spectrum with broadened lines. If the radical is rapidly tumbling the anisotropic effect may be averaged to zero.

A number of gross approximations are made in this simple approach. It is assumed that the radical does not feel any crystal field effects. It is also assumed that the total orbital angular momentum for the system is zero. Inorganic radicals often have significant orbital contributions. These orbital contributions can lead to an anisotropic g value. A more rigorous treatment is available in a number of texts.^{1,2}

Fluorine Containing Radicals Studied in Crystals

Assuming radicals in crystals are locked into a particular orientation by the crystal lattice, it should be possible to determine the ESR spectrum as a function of the external field. In practice a single crystal is mounted so that the angles between the crystal axes and the magnetic field can be varied. If the crystal structure is known, the angles between the molecular axes and the field can then be determined.

Kanzig et al.^{3,4,5,6} have studied radicals produced in single crystals of lithium fluoride as the result of X irradiation at liquid nitrogen temperature. They observed resonances from what they identified as F_2^- and F_3^{-2} molecular ions. They determined the isotropic and anisotropic hyperfine coupling constants and also evaluated the anisotropic g value. From their data they postulated that the unpaired electron resided in a σ^* molecular orbital in the F_2^- and in a π^* orbital in the F_3^{-2} ion. They also reasoned that the F_3^{-2} ion was not linear. Symons⁷ has reconsidered this data in the light of theoretical calculations made for coupling constants of pure 2s and 2p orbitals for a number of atoms including fluorine.⁸ For the F_2^- ion he reasoned that the unpaired orbital consisted mainly of fluorine $2p_z$ orbitals. In the case of F_3^{-2} he felt that the ion was nearly linear and that the unpaired electron occupied a σ^* orbital consisting primarily of the central fluorine $2p_z$ orbital with smaller contributions from the outer fluorine $2p_z$ orbitals. The F_2^- ion has more recently been observed in calcium fluoride⁹ and potassium bifluoride¹⁰ crystals. In both cases it appears to be very similar to the species in lithium fluoride.

Morton has detected radical species occurring in γ -irradiated single crystals of XeF_4 and KrF_4 .^{11,12} He identified these radicals as XeF and KrF . In the case of XeF he observed fluorine and xenon hyperfine structure (Xe^{131} and Xe^{129} have nuclear spins). The radicals appeared to be orientated in the crystal such that the Xe-F bonds were parallel. From the single crystal ESR observations he concluded that the unpaired electron occupied a σ^* molecular orbital consisting mainly of the fluorine $2p_z$ and the xenon $5p_z$ orbitals. Although he wasn't able to resolve any krypton hyperfine splitting (only one isotope of Kr with 11% natural abundance has a nuclear spin), he assumed that KrF was similar to XeF .

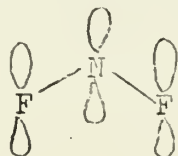
A number of other radicals such as $PF_4^{13,14}$ and PF^{14} have been reported in polycrystalline (powdered) salts. These radicals exhibit isotropic spectra. Generally less information is obtained from powdered samples than from single crystals. Although single crystal studies are the most informative, only a limited number of systems can be studied in this manner.

Fluorine Radicals Studied in Inert Matrices

Another common ESR technique involves the study of radicals trapped in an inert solid matrix. Inert gases such as argon frozen to a solid are often used as matrix materials. The experiment is usually carried out at liquid helium temperature.

Farmer¹⁵ and Kasai¹⁶ have studied the NF_2 radical in a number of matrices. This radical results from the equilibrium dissociation of tetrafluorohydrazine (F_2NNF_2). Both nitrogen and fluorine hyperfine structure was observed. Both authors concluded the radical was non-linear and that the unpaired electron occupied a π^* orbital of b_1 symmetry. This π^* orbital consists primarily of nitrogen and fluorine $2p_x$ orbitals.

The NF_2 radical



The $2p_x$ orbitals are perpendicular to the plane of the nuclei.

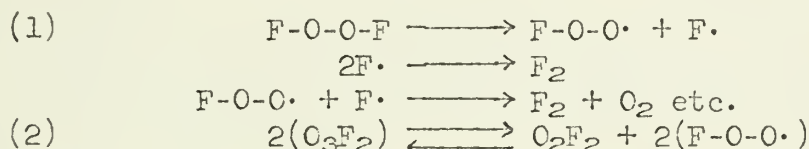
Recently a number of fluorine containing radicals have been observed in irradiated SF_6 matrices.¹⁷

Other Studies

In addition to being a tool for elucidating electronic structure, electron spin resonance is useful for thermodynamic, kinetic, and mechanistic studies. For example the $\text{NF}_2\text{-N}_2\text{F}_4$ equilibrium has been studied in both liquid and vapor states as a function of temperature.^{18,19} Here ESR was being used simply to determine the concentration of NF_2 . Values for the enthalpy of dissociation were obtained which were in excellent agreement with those determined from other physical measurements.

ESR studies of decomposition of a number of reactive oxygen containing fluorine compounds have been made. Neumayer²⁰ has studied the decomposition of peroxydisulfuryl difluoride (FSO_2OOF) and related compounds. He observed a number of paramagnetic species which he attempted to identify. From his results he was able to make some speculations on the bond cleavages involved in the decompositions of these compounds.

Kasai²¹ and Kirchenbaum²² studied the decomposition of the oxygen fluorides O_2F_2 , O_3F_2 , and O_4F_2 . In all cases they observed a radical which they postulated to be OOF . They suggested the following decomposition mechanisms:



Metz²³ found the same radical in studying the photodecomposition of OF_2 . Fessenden²⁴ observed this radical in the spectrum of CF_4 electron irradiated in the presence of oxygen. Fessenden²⁴ and Metz²⁵ were able through the use of oxygen¹⁷ enriched samples to positively identify this radical as $\cdot\text{OOF}$ (oxygen¹⁷ has a nuclear spin). They concluded that the unpaired electron was localized mainly in oxygen 2p orbitals. Their results indicated that the electron was not equally shared between the two oxygens.

Conclusion

Electron spin resonance is a very sensitive detector for unpaired spins and radicals are often very reactive and difficult to obtain in large concentrations. For these reasons it is perhaps the most powerful method for studying these species. However, like any physical method it is best when used in conjunction with other methods.

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SULFUR BRIDGED COMPOUNDS AND THE MAGNETIC EXCHANGE INTERACTION

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Introduction

The reaction of an iron carbonyl with an organodisulfide $(\text{CH}_3)_2\text{S}_2$ or a mercaptan CH_3SH was reported as early as 1928.¹ A general feature of the reaction was the cleavage of the sulfur linkage in the organodisulfide to produce a diamagnetic compound formulated as $\text{Fe}_2(\text{CO})_6\text{S}_2\text{R}_2$; identical to the product formed by the mercaptan. Work was continued under the supervision of Hieber using $\text{Fe}_3(\text{CO})_{12}$ and various organodisulfides, polysulfides, and mercaptans.^{2,3} Structural evidence first appeared in 1960 when dipole moments and infrared spectra were reported for $[\text{Fe}(\text{CO})_3\text{S}]_2$, $[\text{Fe}(\text{CO})_3\text{Se}]_2$, and $[\text{Fe}(\text{CO})_3\text{SC}_2\text{H}_5]_2$.⁴ These moments favored a C_{2v} symmetry quite similar to the dimeric structures of $\text{Co}_2(\text{CO})_8$ ⁵ and $\text{Fe}_2(\text{CO})_9$.⁶ In the space of the next five years, three crystal structures were solved and clearly showed the presence of bridging sulfur groups in $[\text{Fe}(\text{CO})_3\text{SC}_2\text{H}_5]_2$,⁷ $[\text{Fe}(\text{CO})_3\text{S}]_2$,⁸ and $\text{Fe}_3(\text{CO})_9\text{S}_2$.⁹ Recent advances in metal carbonyl chemistry have provided new and interesting compounds with bridging sulfur groups. Most compounds are diamagnetic except for the tetra-bridged vanadium compounds $[\text{C}_5\text{H}_5\text{V}(\text{CH}_3\text{CO}_2)_2]_2$,¹⁰ $[\text{C}_5\text{H}_5\text{V}(\text{S}_2\text{C}_4\text{F}_8)]_2$,¹¹ and $[\text{C}_5\text{H}_5\text{V}(\text{SCH}_3)_2]_2$ ¹² which show anomalous temperature dependent magnetic properties. More commonly known systems which exhibit the same type of behavior are $[\text{Fe}(\text{o-phen.})_2\text{OH}_2]_2$ ¹³ and $[\text{Cu}(\text{CH}_3\text{CO}_2)_2\text{OH}_2]_2$.¹⁴ Anomalous magnetic properties of this type are a consequence of a more general phenomenon called the "antiferromagnetic exchange interaction."¹⁵

Organometallic Sulfur Complexes

A list of the known compounds having bridging sulfur groups (with the exception of $\text{C}_5\text{H}_5\text{CoS}_2\text{C}_4\text{F}_6$) is provided in Table I. The interest in the compounds has been mainly preparative with structures postulated on the evidence of infrared, nuclear magnetic resonance, mass spectrum, and magnetic studies. King has separated the geometrical isomers of $[\text{Fe}(\text{CO})_3\text{SCH}_3]_2$ into syn and anti forms.¹⁶ Isomers depending on the relative orientations of the $\pi\text{-C}_5\text{H}_5$ groups in $[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{SCH}_3]_2$ have also been postulated.¹¹ Only three derivatives of the sulfur complexes have been reported: $\text{Fe}_2(\text{CO})_5\text{P}(\text{C}_6\text{H}_5)_3(\text{SC}_2\text{H}_5)_2$,¹⁷ $\text{Fe}_2(\text{CO})_4[\text{P}(\text{C}_6\text{H}_5)_3]_2(\text{SC}_2\text{H}_5)_2$,¹⁷ and a 2,2,1-heptadiene 2,5 complex formulated as $\text{Fe}_2(\text{CO})_4\text{C}_7\text{H}_3(\text{S}_2\text{C}_2\text{H}_5)_2$.¹⁸ King and Stone have utilized the cleavage properties of organodisulfides to prepare a binuclear compound $\text{Fe}_2(\text{CO})_6\text{RS}(\text{CH}=\text{CH}_2)$, ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_6\text{H}_5, \text{CH}=\text{CH}_2$) which contains a bridging ethylene group.¹⁹

Transition Metal Complexes

Many compounds of the transition metals with the ligands $\text{S}_2\text{C}_2\text{R}_2$ ($\text{R} = \text{C}_6\text{H}_5, \text{CF}_3, \text{CN}$) are well known. Davison, Edelstein, Holm, and Maki²⁰

have investigated the square planar complexes $M[S_2C_2(CF_3)_2]_2^z$ where $z = -2$, $M = Pd, Pt, Co$; $z = -1$, $M = Pd, Pt, Co, Fe$; $z = 0$, $M = Ni$. The above complexes are the product of electron transfer reactions affected both chemically and electrochemically. The same authors also report for $R = CN$, $Z = -k$, $M = Pt, Pd$, two complexes which are diamagnetic and weakly paramagnetic (1.1 BM.), respectively in the solid state, but are both paramagnetic in solution having $\langle g \rangle$ values of 2.0238 and 2.042. The nickel complex of this series shows a room temperature magnetic moment of 1.0 BM., but a solution $\langle g \rangle$ value of 2.0633. Magnetic studies by Wieher, Melby and Benson on the system $M[S_2C_2(CF_3)_2]_2$, where $M = Fe, Ni, Pd, Pt$, indicate intermolecular antiferromagnetic exchange in the solid state.²¹ In accord with complexes of this type, Enemark and Lipscomb²² have solved the crystal structure of the diamagnetic complex $Co[S_2C_2(CF_3)_2]_2$ and found the magnetic property to be a result of dimer formation in the solid state. Other studies by Gray and Billig²³ on the system $M(S_2C_6H_3CH_3)_2^{-1}$, where $M = Cu, Ni, Co, Fe$, by electron spin resonance reveal the presence of M^+ species and two dithiolate radical anion moieties.

Magnetic Properties

Metal-metal bonds have been forwarded in most of the organometallic sulfur complexes to explain the diamagnetism of the compounds. The existence of anomalous magnetic properties in the vanadium compounds raises the question of whether metal-metal bonds form or whether this is the result of both direct and indirect exchange processes similar to exchange theories proposed by Kramer,²⁴ Van Vleck²⁵ or Anderson.²⁶

There are two basic methods used to measure magnetic properties. Induction methods measure the magnetic inductance within a sample by induction bridges,^{27,28} permeability bridges,^{29,30} and oscillators.³¹ Force methods measure the force exerted on the sample by Faraday,^{32,33,34} Curie Cheneveau,³⁵ Guoy,³⁶ and Rankine³⁷ balances. Figgis and Lewis^{38,39} have extensively reviewed the magnetic properties of the transition metal compounds. Magnetic moments obtained by experiment may be interpreted in terms of the spin only value $u = g\sqrt{S(S+1)}$, spin-orbit coupling $u = \sqrt{4S(S+1) + L(L+1)}$, and ligand field perturbations with spin orbit coupling $u = \sqrt{4S(S+1)} - (1 - 4\lambda/10 Dq)$. These equations may be derived from the form of the magnetic susceptibility X and the interested reader is referred to Ballhausen⁴⁰ or Figgis.⁴¹ Most paramagnetic compounds obey the well known Curie Law $X = C/T + B$ where T is the absolute temperature and C and B are constants. Application of the above equations adequately describe most magnetic behavior with the exception of two cases: 1) low temperature anomalous behavior and 2) magnetic exchange interactions.

The anomalous properties of ferromagnetism, antiferromagnetism, and ferrimagnetism have been reviewed by Goodenough.⁴² The theories are beyond the scope of this seminar, but have been classically evaluated in terms of the Weiss Molecular Field,⁴³ and the Heisenberg Exchange Interaction.⁴⁴ Ferromagnetism may be interpreted as a long range cooperative phenomenon which produces a large spontaneous magnetization at the Curie temperature T_c . Antiferromagnetism occurs when sublattices are alternately parallel and antiparallel to the applied field at the critical Néel temperature T_n .^{45,46} Ferrimagnetism may also be discussed in terms of

the sublattice theory where the moments in the two sublattices are no longer directly opposed.⁴² Predicting when the above properties will occur has been a lively topic in the literature.⁵⁷ Goodenough⁴² has postulated several exchange mechanisms which consider the symmetry and occupation of the metal d-orbitals of the cations as well as the presence of intervening non-magnetic anions. Electron spin exchange occurs by a correlation mechanism which postulates partial bond formation on each side of an anion and a delocalization process that allows electrons to drift from one cation to another. The 180° cation-anion-cation interactions are found to be predominant in the perkovskite structures of LaFeO_3 and LaCrO_3 as well as the rock salt structures of various metal oxides.⁴² The 90° cation-anion-cation interactions are important in the rutile and corundum lattices of the metal oxides and fluorides.⁴² These are all superexchange effects and are not to be confused with direct exchange made possible by metal-metal interactions.

The most common exchange phenomenon encountered in transition metal compounds is the antiferromagnetic coupling of electron spins. Experimental indication of this phenomenon is the presence of an abnormally low, temperature dependent magnetic moment. The symbol J is used to express the energy barrier between coupled and uncoupled spin states. Three cases must be distinguished: 1) Within the metal atom or ion, there exists an uncoupled state within thermal range of a coupled state. (The term coupled refers to a net spin pairing effect while the term uncoupled refers to a spin free state.) The relative energy separation will be a function of the crystal field splitting parameter Δ and the mixing of levels by spin-orbit perturbations.⁴¹ Williams, Smith and Staufer⁴⁷ have investigated some six coordinate cobalt(II) complexes having magnetic moments between the high spin values of 4.8-5.6 BM. and the low spin values of 1.7-2.0 BM. The anomalous magnetic properties are due to the crossing over a 4T_1 state and 2E state with increasing temperature; in this case Δ is temperature dependent. 2) The overlap of orbitals in dimeric molecules permit antiferromagnetic exchange. Copper acetate hydrate,⁴⁸ tetraphenanthroline dihydroxy diferric chloride,¹³ and several vanadyl complexes with tridentate ligands^{52,53} show singlet ground states with thermally accessible triplet states lying approximately 300 cm^{-1} above. In all cases, the susceptibility can be described by the equation for exchange coupled pairs as given by Bleany and Bowers.⁴⁹ 3) Interactions between paramagnetic species in the solid state due to weak intermolecular forces give rise to antiferromagnetic exchange. Examples of this type may be found in the square planar complexes studied by Wieher, Melby and Benson.²¹

Conclusion

Little is known about the organometallic compounds that have bridging sulfur groups. The derivative chemistry has not been investigated and the bonding is not clear. Electronic spectroscopy should be a valuable tool in learning something about the bonding because several of the complexes are deeply colored. Mössbauer studies would be valuable in clarifying the environments of the metal nuclei and their formal oxidation states.

Most of the compounds are diamagnetic due to formation of "metal-metal" bonds. This might be the result of an antiferromagnetic exchange interaction having a rather large J value; both superexchange and direct exchange contributing to the spin coupling. Perhaps high temperature magnetic work or electron spin resonance studies at elevated temperatures would reveal this behavior. Clearly, much work should be done on putting the qualitative mechanism of magnetic exchange on a more quantitative and hence predictable basis.

Table I

<u>Reactant</u>	<u>Product</u>	u_{eff}^{\dagger}	<u>References</u>
$\text{Fe}(\text{CO})_5$	$[\text{Fe}(\text{CO})_3\text{SR}]_2^*$	-	1,2,3,4,7
$\text{Fe}_3(\text{CO})_{12}$	$[\text{Fe}(\text{CO})_3\text{SR}]_2^*$	-	1,2,3,4,7, 51,55
$\text{FeSO}_4 + \text{NO}$	$[\text{Fe}(\text{NO})_2\text{SR}]_2^*$	-	4,50
$\text{Fe}_3(\text{CO})_{12}$	$[\text{Fe}(\text{CO})_3\text{S}]_2$	-	8
$\text{C}_5\text{H}_5\text{Co}(\text{CO})_2$	$[\text{C}_5\text{H}_5\text{CoSCH}_3]_2$	-	19
$[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$	$[\text{C}_5\text{H}_5\text{Fe}(\text{CO})\text{SCH}_3]_2$	-	19
$\text{C}_5\text{H}_5\text{V}(\text{CO})_4$	$[\text{C}_5\text{H}_5\text{V}(\text{CH}_3\text{CO}_2)_2]_2$	1.49 BM.	10
$\text{C}_5\text{H}_5\text{V}(\text{CO})_4$	$[\text{C}_5\text{H}_5\text{V}(\text{SCH}_3)_2]_2$	0.90 BM.	11,12
$[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$	$[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{SCH}_3]_2$	-	11
$\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3\text{H}$	$[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{SCH}_3]_2$	-	56
$\text{C}_5\text{H}_5\text{V}(\text{CO})_4$	$[\text{C}_5\text{H}_5\text{V}(\text{S}_2\text{C}_4\text{F}_6)]_2$	0.58 BM.	11,12,55,56
$[\text{C}_5\text{H}_5\text{Mo}(\text{CO})_3]_2$	$[\text{C}_5\text{H}_5\text{Mo}(\text{S}_2\text{C}_4\text{F}_6)]_2$	-	55,10
$[\text{C}_5\text{H}_5\text{Cr}(\text{CO})_3]_2\text{Hg}$	$[\text{C}_5\text{H}_5\text{Cr}(\text{S}_2\text{C}_4\text{F}_6)]_2$?	11,55
$\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{NO}$	$[\text{C}_5\text{H}_5\text{MoNO}(\text{S}_2\text{C}_4\text{F}_6)]_2$	-	55
$\text{C}_5\text{H}_5\text{Co}(\text{CO})_2$	$\text{C}_5\text{H}_5\text{CoS}_2\text{C}_4\text{F}_6$	-	55,54
$[\text{C}_5\text{H}_5\text{W}(\text{CO})_3]_2$	$[\text{C}_5\text{H}_5\text{W}(\text{CO})\text{S}_2\text{C}_4\text{F}_6]_2$	-	55,10

* $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$

† Room temperature moment.

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COMPLEXES OF DERIVATIVES OF L-CYSTEINE

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Introduction

Although the complexes of cysteine have been extensively studied,¹⁻⁴ the complexes formed with certain types of its derivatives have received considerably less attention.

Thioether Derivatives of Cysteine

A principal point of interest in complexes of these derivatives with divalent metal ions is the possibility of sulfur coordination in addition to coordination of the amine and carboxyl groups. Solution studies of complexes of simple derivatives of L-cysteine and of methionine (HMT) suggested that complexation with divalent, first-row transition metal ions does not involve coordination of the sulfur atom.^{5,6,7} However, another study suggested that sulfur coordination was present in the complex $\text{Cu}(\text{Mt})_2$ in solution.⁸ The $\text{Ag}(\text{I})$ ion does coordinate to the thioether sulfur atom in $\text{Ag}(\text{Mt})_2^-$ but not with the amine and carboxyl donors as well.⁹

Recently the possibility of sulfur coordination in the solid complexes has been investigated. Infrared spectra⁴ as well as magnetic moments and visible spectra¹⁰ were employed. It was concluded that no sulfur coordination was present in the bis complexes studied. However, sulfur coordination was postulated to exist in the complexes $\text{Cu}(\text{Mt})(\text{ClO}_4)$ and $\text{Ni}(\text{Mt})(\text{ClO}_4)$.¹⁰ The isolation of the complex $[\text{PtCl}_2(\text{HMT})]$ indicated that the platinum(II) ion exhibits a preference for coordination to the thioether sulfur atom.¹¹ Ultraviolet, infrared, and visible spectra suggest that these general conclusions are valid for the complexes of certain thioether derivatives of cysteine as well.

Reactions of Bis(S-tritylcysteine) Complexes

The carbon-sulfur bond of the type $\text{Ar}_3\text{C-S-}$ ($\text{Ar} = \text{aryl}$) in certain organic compounds has been shown to undergo cleavage by $\text{Ag}(\text{I})$ and $\text{Hg}(\text{II})$ ions.¹²⁻¹⁵ The effect of these heavy metal ions on the bis complexes of S-tritylcysteine with copper(II) and nickel(II) has been studied. Attempts were made to oxidize the remaining cysteine ligand and to characterize the resulting heterometallic complexes of cysteine.

Bis(Cysteine Ethyl Ester) Nickel(II) Complex $\text{Ni}(\text{Etc})_2$

Studies of the complex $\text{Ni}(\text{Etc})_2$ and the analogous complex of the methyl ester have been carried out in aqueous solution. Formation constants and rate constants for their hydrolysis reaction with base were determined.¹⁶⁻¹⁸ Chelation via the amine and thiol groups was proposed.¹⁷

The solid complex $\text{Ni}(\text{Etc})_2$ has been isolated and its visible spectra studied. Coordination of the carbonyl oxygen to the nickel, if present, should be manifested in the infrared spectrum.^{19,20} This complex undergoes addition reactions at the coordinated thiol sulfur atom.

Thioether Derivatives of Cysteine Ethyl Ester

Busch and co-workers have shown that β -mercaptoethylamine complexes of nickel(II) undergo addition reactions with certain organic halides.^{21,22} They have also investigated this reaction with other ligands.^{21,23}

The complex $\text{Ni}(\text{Etc})_2$ readily undergoes a similar reaction with benzyl chloride, benzylthiomethyl chloride, and trityl chloride. The resulting complexes have been studied. In the case of benzylthiomethyl chloride, this reaction provides a convenient preparation of the resulting ligand.

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Diane Tullius

May 16, 1967

Introduction

Raman spectroscopy was quite popular after its discovery in 1928 and in the 1930's, but as limitations were encountered and commercial infrared spectrometers became available, it was used less and less. Classical Raman has certain advantages over infrared spectrometry, such as permitting the use of H₂O solutions and the relatively easy obtaining of low frequency vibrations.^{1,2} If the limitations encountered in classical Raman could be overcome, many areas for research would be opened up.

Limitations of Classical Raman

1. The Raman effect arises from a second order process, thus one must put in a great deal of energy in order to obtain a spectrum.²
2. Colored samples that have the color yellow or any color with a longer wavelength can not be run with the most common source, Hg (4358 Å), because they absorb so much of the light rather than scatter it.^{1,3,17} Lower energy sources have been used,⁴ but Raman intensity is directly proportional to ν_0^4 ,^{5,17} and the photographic plates are not as sensitive in that region of the spectrum.⁶
3. Fluorescence from samples, cells, and/or impurities sometimes masks part of or completely wipes out the spectrum.^{1,7}
4. It takes up to tens of hours to record a spectrum,¹ and unstable materials may decompose.
5. Photodecomposition is caused by the Hg line or stray light around it.^{1,7}

Properties of Lasers in View of the Above Limitations

The output of a laser is a very intense, well-collimated, monochromatic coherent beam of light.

The output of the gas lasers used so far in Raman spectroscopy is of the order of milliwatts whereas the Hg-lamp has an output of watts. This output from the laser is concentrated though into a beam of 0.5 mm in diameter⁸ which diverges very little, thus the energy flux through a given volume of sample is greater than indicated by its output. The laser beam can be focused so as to illuminate volumes as small as 10^{-7} to 10^{-8} liters.¹ This facilitates the use of small samples, but the narrowness of the beam proves to be a disadvantage when trying to obtain Raman spectra of gases because of the limited quantity that can be illuminated.^{6,9}

The amount of light passing through a sample can be greatly increased (400 times)^{5,18} by placing the sample inside the laser cavity if the sample is "non-lossy."⁵ Exposure time should be cut down, and thus worry about the instability of a compound decreased.

The monochromaticity of the laser light (0.05 cm^{-1} or less, He-Ne; 0.15 cm^{-1} , A⁺; 0.20 cm^{-1} , water-cooled Hg lamp)⁶ cuts down on the chances of absorption, fluorescence, and/or photodecomposition⁹ because of the

decrease in stray light. The narrowness of the spectral width of the beam from a laser also makes it a better source for high resolution work.^{6,9}

Applications Facilitated by Lasers

In order to test the feasibility of lasers for Raman work and perfect the apparatus lasers were first used on substances whose Raman spectra had already been recorded by using the Hg-lamp.^{5,8,9,10,11} The first published attempt to use a laser for Raman spectroscopy appeared in 1962,¹¹ and now you can find articles where it is used routinely and not even mentioned in the title of the article.

The following are some applications that were made possible or facilitated by lasers:

1. In order to get some idea of the force constant of the M-X bond in the square planar complexes, MX_4^{n-} , where X = Cl, Br, or I when M is Au or Pt and X = Cl or Br when M is Pd, the Raman spectra of these complexes were obtained from the salts K_nMX_4 , even though most of them are black or red-brown powders. Assignments were made on the basis of polarization studies on KAuI_4 , and the frequency of the A_{1g} mode was used to obtain a rough force constant.³
2. The angular dependence of some of the Raman active modes of benzene were studied at angles from 0° to 180° with respect to the exciting beam and were found to fit the theory that is the basis for determining the symmetry of the bands.¹²
3. High resolution work on low pressure gases was developed to the point that resolution was limited only by the Doppler effect due to molecular motion and the time required to obtain a spectrum was of the same magnitude as that for a Hg-lamp. This was brought about by the use of a multipass cell and a new, more sensitive film. Because of the high degree of polarization of the exciting line, the Rayleigh line could be blanked out by viewing the scattered light parallel to the electric vector of the exciting light and the depolarized rotational spectrum could still be recorded.^{6,9}
4. The high degree of polarization and control over it has facilitated oriented crystal work and has cleared up anomalous polarizability (α) values in crystals caused by depolarization of non-lasing light. The well polarized laser light of the commercial Cary laser unmodified gave good spectra for bis(dimethylsulfide)dibromo platinum(II). Three lines were found in the spectrum. Two could be assigned by analogy to previous work to the X-M-X symmetrical stretch (215 cm^{-1}) and the S-M-S symmetrical stretch (341 cm^{-1}). On the basis of how their intensities changed as the crystal was rotated, the third band was assigned to an S-M-S bend (143 cm^{-1}).¹³
- Anomalies in the polarization of the A_{1g} mode in calcite due to depolarization of the incoherent non-laser light were removed when the coherent light from a laser was used.¹⁴
5. Finally some examples of improvement in fluorescence are 9,10 dibromoanthracene and indene. 9,10 dibromoanthracene's spectrum is completely wiped out under Hg light; indene's spectrum is only partly covered. 9,10 dibromoanthracene's spectrum can be seen using a He-Ne laser, and indene's is improved.⁷

Further Unexplored Areas

It has been suggested that electronic Raman of far infrared transitions, i.e., d-f transitions in rare earths, be studied.¹⁵ Recently a Raman line (523 cm^{-1}) was recorded for Si, and it was suggested that perhaps the Raman spectra of metals could be recorded.¹⁶

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APPLICATIONS OF CRYSTAL FIELD THEORY TO SPECTRA OF SOME TETRAGONAL COMPLEXES

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May 23, 1967

Introduction

Crystal field theory, developed by Becquerel,¹ Bethe,^{2,3} and Kramers,⁴⁻⁶ was first applied to the spectra of aqueous transition metal ions by Ilse and Hartmann.⁷⁻¹²

The purpose of this seminar is to discuss briefly the mathematical formulation of crystal field theory for tetragonal molecules and to review the development of the theory in its application to explaining electronic spectra. It is impossible to cover thoroughly every calculation that has been done on tetragonal molecules, but several representative examples will be discussed. The examples chosen are primarily square planar or tetragonal bipyramidal complexes of $3d^n$ ions. A more complete listing is given in the form of references.

Formulation¹⁴⁻¹⁸

The quantum mechanical treatment of the effect of the crystal field in a tetragonal complex begins with the formulation of the Hamiltonian:

$$\mathcal{H} = \sum_j \left\{ -\frac{\hbar^2}{2m} \nabla_j^2 - \frac{Ze^2}{|r_j|} + \xi(r_j) \ell_j \cdot S_j \right\} + \sum_{k>j} \frac{e^2}{|r_{jk}|} + v_{CF} \quad (1)$$

The first four terms are exactly those of the free ion; the last term, v_{CF} , expresses the effects on the metal of the superimposed potential field of the ligands. This term depends on the positions of the ligands surrounding the metal and may be written in terms of the spherical harmonics.¹³

$$v_{CF} = e^2 \sum_{i=1}^N \sum_{l=0}^{\infty} \sum_{m=-l}^l \frac{4\pi q_i}{2l+1} \left(\frac{r_<^l}{r_>^{l+1}} \right) Y_l^m(\theta_i, \phi_i) Y_l^m(\theta_j, \phi_j) \quad (2)$$

where: $Y_l^m(\theta, \phi)$ are the spherical harmonics (see Fig. 1). q_i is the charge on the ligand. $r_<(r_>)$ is the shorter (longer) of the radial vectors connecting the origin to the electron and to the ligand. e is the charge of the electron. N is the number of ligands.

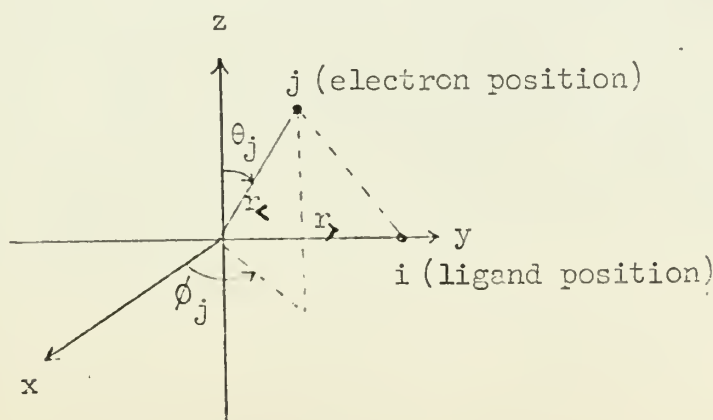


Fig. 1

For d-electrons ($\ell = 2$) we find that the only non-zero terms, by the nature of the spherical harmonics, are the following

$$v_{CF} = \alpha Y_0^0 + \beta Y_2^0 + \gamma Y_4^0 + \delta (Y_4^4 + Y_4^{-4}) \quad (3)$$

where α, β, \dots are constants. Y_0^0 has no angular dependence and $Y_4^{\pm 4}$ is independent of the axial ligands. Thus equation (3) may be rewritten as follows:

$$v_{CF} = \alpha Y_0^0 + [\epsilon Y_4^0 + \delta (Y_4^4 + Y_4^{-4})] + [\beta Y_2^0 + \gamma' Y_4^0] \quad (4)$$

$$v_{CF} = v_S + v_{Oh} + v_T \quad (5)$$

where: v_S is the spherically symmetric perturbation.

v_{Oh} is the octahedral perturbation.

v_T is the tetragonal perturbation.

Applying these perturbations successively from left to right ($v_S > v_{Oh} > v_T$) enables one to consider the tetragonal complex as octahedral with an axial perturbation.

In the octahedral field we define the radial parameter Dq , which describes the octahedral splitting.

$$Dq = \frac{1}{6} q e^2 \int_0^\infty (R_{3d})^2 r_{<}^4 / r_{>}^5 r^2 dr = \frac{1}{6} q e^2 \left\langle \frac{r_{<}^4}{r_{>}^5} \right\rangle \quad (6)$$

where R_{3d} is the radial part of the 3d wave function. As the field is distorted along the z-axis, we must define two new parameters, D_s and D_t , arising from Y_2^0 and Y_4^0 respectively, which describe the splitting of the octahedral levels.

$$D_s = 2/7 e^2 [q_{xy} \langle r_{<}^2 / r_{>}^3 \rangle_{xy} - q_z \langle r_{<}^2 / r_{>}^3 \rangle_z] \quad (7)$$

$$D_t = 2/21 e^2 [q_{xy} \langle r_{<}^4 / r_{>}^5 \rangle_{xy} - q_z \langle r_{<}^4 / r_{>}^5 \rangle_z] \quad (8)$$

where the subscripts xy and z refer to the effective field of the xy-plane and the z-axis respectively.

Applications of the Theory

The success of Ilse and Hartmann^{7,8} in describing the spectrum of $Tl(OH_2)_6^{3+}$ suggested to J. Bjerrum, et al.,¹⁹ that crystal field theory might be used to determine the structure of Cu(II) complexes in solution. Postulating square planar, tetrahedral, octahedral and tetragonal bipyramidal structures, they calculated transition energies based on these models.²⁰ Varying μ , the effective dipole moment of the ligand, and R, the copper-ligand distance, within reasonable limits, they calculated the energies of the highest frequency transitions for the four geometries mentioned above. Only square planar and tetragonal bipyramidal geometries were consistent with experimental results. Further analysis demonstrated that both the tetramine and aquo complexes of Cu(II) are tetragonal bipyramids with solvent water coordinated along the z-axis. Spectral predictions with this model were very good.

Ballhausen^{21,22} calculated matrix elements for d^n in tetragonal fields. Calculated transitions for trans-Ni(en)₂²⁺ were close to those observed (<15% error). However, splitting of the T and E states in the D_{4h} field was not sufficient to permit resolution of six peaks; only three were observed.

The same difficulty was encountered by Belford, *et al.*,²³ in their work with Cu(II) chelates and by Maki²⁴⁻²⁶ in her extensive calculations involving Ni(II) chelates. Maki carried out calculations for square-planar complexes in the usual manner, using Slater orbitals and allowing for configuration interaction. As a final step in the determination of numerical values of the \mathcal{H}_i 's, a choice of values for the parameters, μ (or q) and R , was made. Those values were chosen for a particular compound which gave the best overall fit to the spectrum. Following closely the technique of Bjerrum, *et al.*,^{19,20} Maki calculated transition energies for bis-*o*-phenylenediamine nickel(II) chloride, bis(acetylacetonate)nickel(II), etc., assuming the same four geometries. In all cases the number and positions of calculated transitions favored square planar or tetragonal bipyramidal geometries. The results were self-consistent for the parameter values chosen. For example, the value of the dipole moment of pyridine used gave consistent results over a series of compounds.

Crystal field theory has been strikingly successful in interpreting spectra of complexes in which resolution of tetragonal splitting is observable. For example, Ballhausen and Moffitt²⁷ used crystal field theory to assign the transitions of the polarized spectrum of trans-Co(en)₂Cl₂⁺, which had been observed to be strongly dichroic.²⁸ Yamatera²⁹ had some success in fitting the transitions by crystal field considerations but suffered from an attempt to use Slater free ion radial wave functions and ligand dipole moments. Piper and co-workers^{30-34,43} in a series of papers probed the problem more thoroughly. Noting that the splitting of the ¹T₁ levels in trans-CoL₄X₂⁺ was a function of Dt only, they defined a new parameter $Dt' = -4/35[W - (10 Dq - C)_{xy}]$ where W is the lowest energy transition in the tetragonal complex (¹A₁ → ¹E_g) and $(10 Dq - C)_{xy}$ is the lowest energy transition of the parent octahedral complex (¹A₁ → ¹T₁). In cases where the ¹T₁ band splitting was not resolved, they assumed that the position of the band maximum in the tetragonal complex was midway between the ¹A₁ → ¹A₂ and ¹A₁ → ¹E_g^a transitions. This approximation tacitly assumes that the intensities of the two transitions are equal. With these assumptions, they compiled a large table of values of Dt' and Dq' for Co(III) and Cr(III) complexes.

The fact that splitting of the high energy band was not observed necessarily led to approximations of the type just discussed. However, Baker and Phillips³⁵ were able to detect splitting of this band by careful examination of the spectra of several trans-Cren₂X₂ⁿ⁺ complexes. Approximate resolution of these bands was achieved by a Gaussian analysis. Assuming that Dt was positive on the grounds of previous assignments and that D_s was negative since this sign gave consistent results, they calculated Dq, Ds, and Dt for a series of Cren₂X₂ⁿ⁺ complexes. Calculations done by the present author indicate that these assumptions are unnecessary as polarized single crystal spectra should solve the assignment dilemma.

Stanko³⁴ and Dingle³⁶ used polarized single crystal spectra and group theoretical arguments in proposing a vibronic intensity-gaining mechanism

and assigning transitions in tetragonal cobalt^{34,36} and chromium³⁴ complexes. Though assignments of certain bands are in doubt, their arguments are much more convincing than those of some earlier authors. What seems to be needed in this area is a detailed assignment of the vibrational modes of the ground and excited states in order that quantitative statements might be made about band intensities.

The ideal situation for crystal field calculations of this type is to work with a system which exhibits splitting in many bands, for this allows one to check one's parameters.

An extremely successful treatment of two Ni(II) complexes has been carried out by Rowley and Drago.³⁷ These workers determined values for the parameters B, C, Dq, Ds, and Dt in fitting eight peaks of the complexes trans-NiPy₂X₂ (X = Br, Cl) to within 2%. Spin-orbit coupling was neglected, but configuration interaction was taken into account. Assigned transitions were assumed to be correct on the basis of the excellent agreement obtained between calculated and observed bands.

Conclusion

Though Figgis¹⁵ has suggested that molecular orbital theory be used instead of crystal field theory for explaining the spectra of tetragonal complexes, several workers^{23,29} have obtained very similar results using both M.O. and C.F. theory. Crystal field theory neglecting spin-orbit coupling and configuration interaction gives semi-quantitative results which may lead to incorrect assignments.^{40,41} However, calculations considering only configuration interaction may differ from "complete" calculations by only a few per cent³⁹ for 3d electrons and give surprisingly good results even for 4d³⁰ and 5d³⁸ electrons.

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* Indicates calculations including spin-orbit coupling.

SUBSTITUTION REACTIONS OF SELECTED TRIMERIC
PHOSPHONITRILIC CHLORIDE DERIVATIVES: THESIS REPORT

Marlene K. Feldt

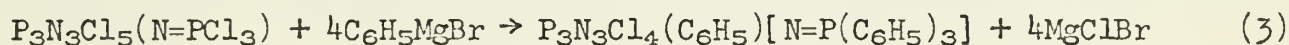
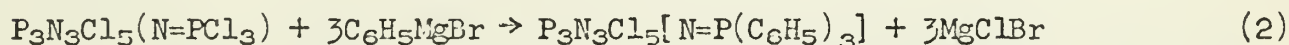
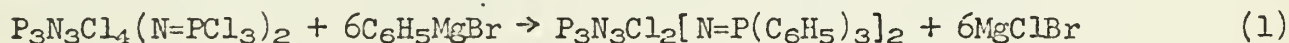
May 25, 1967

This report deals with some specific reactions of various substituted trimeric phosphonitrilic chlorides. Emphasis is placed upon reactions involving amido ($-\text{NH}_2$) and phenyl groups. Further information on phosphonitrilic chemistry can be obtained from any of four review articles.^{7,9,10,11}

To understand the work done in our laboratory, it is first necessary to be familiar with previous work with the amido- and phenyl-substituted compounds. With amines as substituents, much interest has been focused not only on obtaining the complete series of substitution products, $\text{P}_3\text{N}_3\text{Y}_n\text{Cl}_{6-n}$ ($n = 1-6$; Y = primary or secondary amine), but also upon isolation and identification of the possible isomers for the various degrees of substitution. The amines have been classified according to the substitution pattern—geminal or non-geminal—which their reactions with the phosphonitrile follow. Agreement has been reached that methylamine, dimethylamine, and piperidine follow a non-geminal path, whereas aniline, *t*-butylamine, and aziridine follow a geminal path. In the case of ammonia, however, recent investigations^{3,6} have indicated that the substitution is geminal rather than non-geminal, as previously assumed.^{1,4}

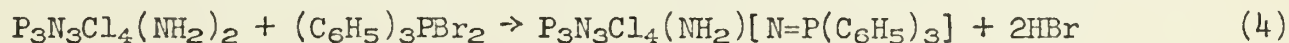
The aryl-substituted phosphonitrilic chloride trimers are usually prepared via a Friedel-Crafts type reaction. Some success has been noted using procedures starting with linear compounds. Organolithium reactions have been completely unsuccessful in the chloride system, and although a successful Grignard reaction has been reported,⁸ this work has not been repeatable.

We have studied the reactions of Grignard reagents with the trichlorophosphazo substituted chlorides which are obtainable from the mono- and diamido compounds. The reactions described by the following equations were investigated:

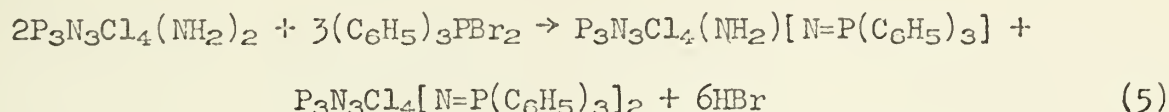


As seen in equation (3) we have successfully phenylated not only the more reactive side chain but also the phosphonitrilic ring itself. This compound has also been claimed as a product of ring rupture and reformation as a consequence of a Grignard phenylation of the tetrameric chloride.²

To investigate further the report⁵ that the reaction described by equation (4) really yielded the monosubstituted compound, a number of



reaction conditions were explored. Of the conditions used, the milder ones gave reaction in terms of equation (4). Under more rigorous conditions, however, the reaction was as shown in equation (5).



All compounds were characterized by analysis and by infra-red and nuclear magnetic resonance spectra. Phosphorus-31 resonances were obtained for all compounds, as well as for a series of comparable linear $\equiv\text{P}=\text{N}-\text{SO}_2$ -compounds, and proton spectra were obtained where applicable.

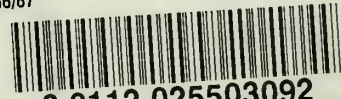
We have shown that a Grignard reaction can be carried out on a substituted trimeric phosphonitrilic chloride without the usual ring cleavage, and that not only the side chain, but the ring as well, can be phenylated. We have also been able to advance further proof for the geminal configuration of the diamidotetrachlorocyclotriphosphazatriene, $\text{P}_3\text{N}_3\text{Cl}_4(\text{NH}_2)_2$. A mass spectral study of bis(triphenylphosphazo)tetrachlorocyclotriphosphonitrile, $\text{P}_3\text{N}_3\text{Cl}_4[\text{N}=\text{P}(\text{C}_6\text{H}_5)_3]_2$, has been carried out. The products of all the reactions have been studied spectroscopically, and the peaks and shifts have been assigned insofar as possible.

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